International Journal of Theoretical Physics, Vol. 19, No. 10, 1980

Nonstationary Quantum Mechanics. II. On the Increase of Entropy with Time

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Received May 19, 1978

On the basis of the discussion in our previous work (T1) and the reexamination of the concept of entropy of a pure quantum state it is shown that a natural explanation of the process of entropy increase exists. A new definition of an entropy operator $\hat{S}$ is given and it is shown that there is not any increase of entropy when one confines oneself to the usual formalism of quantum mechanics and uses this definition. Some other attempts of proving the H theorem are briefly discussed.

1. INTRODUCTION

The discussion in our previous paper (Todorov, 1980; hereafter referred to as T1) showed that the behavior of parts of a larger system is in fact irreversible in time—when the overall system is in a state of definite energy all the subsystems will relax to a stationary state too in the process of their spatial separation. We do not know at present exactly how such a relaxation can be described but the very fact that it is an inherent property of quantum systems is interesting enough and indicates a possible application to nonequilibrium statistical mechanics (even prior to the creation of a precise theory). We have in mind the problem formulated in the title of the present paper.

The problem of entropy increase consists in the definition of some function of time, which is then shown to possess the characteristic properties of entropy known from phenomenological thermodynamics. This is a very old problem of physics and a huge amount of work has been accomplished in the said field from the time of Bolzmann to the present day. In spite of this a rigorous solution has not been found. It became clear in the course of the work that quantities which increase irreversibly with time can be obtained in many different ways. A common feature of all the methods is the use of some assumption which seems quite natural, e.g., the existence of molecular chaos, the possibility to examine coarse-grained distributions, the introduction of terms breaking the symmetry of the Liouville equation with respect to time reversal, or the postulate of correlation weakening in classical and quantum statistical mechanics. As long as no rigorous proofs of these hypotheses exist the problem remains on the addenda.

In this work we shall add a unity to the number of approaches to the said problem. We shall essentially use in our approach the postulate of equilibrium statistical mechanics which says that the thermodynamics of a given system can be obtained from the properties of its microcanonical ensemble (the canonical and grand canonical ensembles are proved to be equivalent to the microcanonical ensemble in this respect; see, e.g., Zubarev, 1971).

We shall show first that one can ascribe definite thermodynamical quantities to the stationary states of the Hamiltonian of many-body systems without coming into contradiction with the well-known results of equilibrium statistical mechanics. Irreversibility will then immediately follow (for a typical nonstationary process) from the results of T1 and the first law of thermodynamics. We shall examine only the quantum case here owing to the basing of our argumentation on the discussion in T1.

2. ON THE EQUIVALENCE OF THE MICROCANONICAL ENSEMBLE TO A STATIONARY QUANTUM STATE

It is well known from phenomenological thermodynamics that definite values of quantities such as the entropy S, temperature T, and so on can be ascribed to stationary many-body systems having energy E and closed in a fixed volume V. It is logical to ask the question: Why should not one think that the stationary quantum states of such systems are the exact realization of the idea of thermodynamical stationary states? (The essential difference between a quantum stationary state and a classical state of fixed energy E will be discussed briefly later on.) Such a thought seems forbidden by the conventional concept which states that the entropy of pure quantum states is always equal to zero. It is interesting therefore to see how this concept has appeared in quantum statistics and what kind of an entropy is really equal to zero in an ensemble of systems in a fixed pure state.

It seems to us that the source of the said opinion can be found in the well-known book of von Neumann (1932). We shall try first to interpret the expression for the entropy of an ensemble of quantum systems obtained there.

Consider an ensemble consisting of M identical copies of an N-particle quantum system, M being a large positive integer and the particles being indiscernible, and let p_i be the probability of finding a fixed system in a stationary state ψ_i of energy E_i. Then $M_i = p_i M$ will be the number of the systems in our ensemble which are in a state ψ_i.

The expression for the entropy S_M of this ensemble obtained in von Neumann's book (1932) is

$$S_M = -Mk_B \sum_i p_i \ln p_i \tag{2.1}$$

where k_B is Bolzmann's constant.

From equation (2.1) it follows that we can ascribe the following average entropy to any system in our ensemble:

$$S = -k_B \sum_i p_i \ln p_i \tag{2.2}$$

There will not be a deep physical sense in such an average entropy in the general case, so that equation (2.2) defines merely some kind of an information entropy of the ensemble. But in the case of a microcanonical ensemble which is basic for statistical mechanics the situation is quite different.

Indeed, as is well known, the microcanonical ensemble consists of systems of energy E_i, $i = 1, 2, \ldots, W$, $E < E_i < E + \Delta E$, where $\Delta E/E \ll 1$, all the probabilities p_i being equal $[p_i = 1/W, i = 1, 2, \ldots, W$, W being the number of independent stationary states of energies inside $(E, E + \Delta E)]$.

In the general case, obviously, the adding of a new copy of our N-particle system to the ensemble will lead to a variation of S_M which is different from the expression (2) (since $p_i \neq p_k$) for "average entropy" S. In the case of a microcanonical ensemble, however, a similar step will lead to a variation of S_M which is almost equal to S when $M \to \infty$, $M_i = p_i M \to \infty$, $W \gg 1$ (the latter condition is always fulfilled when N is a large integer). This is true irrespective of the quantum state ψ_k of the new system [as long as it belongs to $(E, E + \Delta E)$] and it can be immediately verified by examining the initial entropy S_M [see equation (2.1)] and the final entropy $S_{M+1} = -(M+1)k_B \Sigma_i p_i' ln p_i'$, where $p_i = M_i/M \approx M_k/M$ (because of the fact that $M \neq \infty$ we can have only an approximate equality $p_i \approx p_k$ in the general case of arbitrary M, $M \gg 1$, the approximation growing better with the increase of M), $p_i' = M_i/(M+1)$ $(i \neq k)$, $p_k' = (M_k + 1)/(M+1)$.

Indeed,

$$S_{M+1}-S_M=-k_B\left[\sum_i p_i \ln p_i+0(1)\right] \qquad (2.3)$$

where the term 0(1) can be neglected owing to the inequality $W \gg 1$ $[-\Sigma_i p_i \ln p_i \approx -\ln p=-\ln(1/W) \gg 1$ when $W \gg 1]$.

The microcanonical ensemble is a basic postulate of statistical mechanics. This means that the thermodynamical functions have to be calculated using the microcanonical distribution. We are interested in the entropy of an N-particle system with energy varying inside the interval $(E, E+\Delta E)$. It is given by the expression (2.2) for S since this is the average entropy of a system in the microcanonical ensemble (cf. also our subsequent discussion). Our consideration above shows that (2.2) can be interpreted as the thermodynamical entropy of any pure state ψ_i inside the interval $(E, E+\Delta E)$. This fact will be used below in the discussion of the entropy increase with time. Let us stress here that the said fact is a logical consequence of the (inexplicit) physical idea which leads to the postulating of the microcanonical distribution—the equal probabilities are an expression of the concept that practically all the different states ψ_i inside $(E, E+\Delta E)$ are equivalent from the point of view of thermodynamics. Therefore, the above property of the microcanonical distribution is in exact agreement with the already mentioned way of action in phenomenological thermodynamics in which an entropy $S=S(E, V)$ is ascribed to any macroscopical system having an energy equal to E and closed in a volume V, S being a continuous function of E and V.

There exists a seeming contradiction between the fact that we ascribe a thermodynamical entropy $S \neq 0$ to a fixed microstate and equation (2.1), giving $S_M=0$ for an ensemble of systems in a fixed state ψ_i. But what kind of an entropy is S_M? The expression (2.1) for the entropy S_M of the *microcanonical ensemble* is postulated to have a bearing on thermodynamics owing to its physical meaning. This does not mean, however, that any kind of information entropy has a thermodynamical sense. The latter fact is well known (cf., e.g., the discussion in the work of Tisza and Quay, 1963). Still, it is worthwhile to examine the said fact from the point of view of the aims of the present paper. Such a discussion is made even more necessary by the fact that von Neumann's view on the entropy of a pure quantum state continues to be very popular among physicists.

Let us see first how von Neumann tries to find a physical argument in favor of the concept that $S_{\psi_i}=0$ for a fixed pure state ψ_i. He shows in Chapter V of his cited book (von Neumann, 1932) that any quantum state

ψ_i can be transformed into any other state ψ_k if a series of some kind of measurements is effected. (purely abstract; no concrete prescription is offered). In the case of $E_i \neq E_k$ the energy difference $E_i - E_k$ can be taken from a purely mechanical process, no thermal energies being exchanged, so the final entropy should be the same for all ψ_i according to von Neumann and it can be normalized to zero.

Leaving aside the problem for the *actual* possibility of the said measurements we nevertheless have to say that the above statement is simply wrong in the general case since when we have, e.g., a system with a fixed volume the important moment in the discussion of entropy variation is the very fact of the variation of the internal energy of the said system and not what has caused it. For instance, when a missile passes through some gas the latter will be heated owing to the transformation of purely mechanical (kinetic) energy into energy of the thermal motion and the entropy of the gas will increase. But let us turn to the formal deduction of equation (2.1) in Chapter V of von Neumann (1932).

Consider an ensemble of M systems which are identical in any respect with the exception of the quantum state which can be different for the different members of the ensemble. Let the corresponding probabilities be p_i, $\Sigma_i p_i = 1$. We assume that any system of the ensemble is closed in a very heavy box with adiabatical (isolating) walls, the mass of the boxes being much larger than the mass of the gas which they contain and all the characteristics of the boxes being the same. All these boxes are held in another box $\bar{K}$, the volume $\bar{V}$ and the temperature T are such that the classical gas formed by our M boxes can be treated as an ideal gas with thermodynamical parameters $\bar{V}$, T. That part of our ideal gas which contains the $M_i = p_i M$ systems in a stationary state ψ_i can be separated from the rest with the help of a wall penetrable for all states ψ_k, $k \neq i$, and impenetrable for ψ_i, the final volume of the i gas being equal to the volume $\bar{V}$ of $\bar{K}$. The same can be done with all k gases, no thermal energies being involved in these processes, so we shall have in the end ideal classical gases containing $M_1 = p_1 M$, $M_2 = p_2 M, \ldots$ molecules, each of which is closed in the same volume $\bar{V}$. The corresponding volumes are then compressed isothermally to $V_1 = p_1 \bar{V}$, $V_2 = p_2 \bar{V}, \ldots$ in which process the entropy of the total system increases with $k_B \Sigma_i M_i p_i \ln p_i$. In the end, all states ψ_i are reduced to the same state ψ with the help of the said hypothetical series of quantum measurements. No variation of entropy exists in the latter process according to von Neumann. Because of the fact that the entropy of the ψ gas is assumed to be equal to zero and having in mind the said total increase of entropy after the compression we see that the entropy of the ensemble of systems characterized with the set of probabilities $\{p_i\}$ has to be given by equation (2.1).

Thus it seems that the assertation $S_\psi = 0$ is really necessary for the proof of equation (2.1). We shall show that this is not so. Indeed, the above procedure is almost identical to the one in which the entropy S_m of mixing of ideal gases at the same temperature T is obtained [see, e.g., example No. 5 in Chapter 2 of Kubo's book (1968)]. The value S_m precisely coincides with the expression (2.1) for S_M, $M_i = p_i M$ being again the number of molecules of the ith ideal gas and M the total number of the molecules. The only difference between the two procedures is that in the second case we start from volumes $V_i = p_i \bar{V}$ inside which are our ideal gases at the same T and pressure P, then open them, so that the gases can mix in the total volume $\bar{V}$ and afterwards the same procedure of adiabatical separation of the gases and isothermal compression back to V_i is effected and the same result (2.1) is obtained. Consequently, we can do absolutely the same in the case when the ith ideal gas consists of boxes containing quantum systems in stationary states ψ_i and come to the result (2.1) without the assumption $S_\psi = 0$. Thus the total entropy (2.1) of a quantum ensemble is in fact the mixing entropy of ideal classical i gases.

One may ask the following natural question here: If the assertion $S_\psi = 0$ about the thermodynamical entropy is nonphysical then why do the two methods give the same result for S_M?

The answer is simple. The reduction of all states ψ_i to ψ is a superfluous step in von Neumann's procedure and this unnecessary step is neutralized by the nonphysical declaration that $S_\psi = 0$. Indeed, the aim of both procedures examined above is the reversible annihilation of an unknown amount of mixing entropy with an equal amount (but of the opposite sign) of thermodynamical entropy which will be known in the end of the process. In the first procedure this is accomplished by the moment in which all the i gases are compressed isothermally to $V_i = p_i \bar{V}$. The fact that these gases still possess a property (the quantum state ψ_i) which makes them discernible from the point of view of thermodynamics has no more any significance: We have accomplished the necessary reversible separation which gives the exact value of the mixing entropy, the entropy connected with the thermal motion of the boxes being the same as in the initial moment (it is not affected by the existence of impenetrable walls if the total volume and the pressure are the same) and no mixing entropy exists any longer. So it is not necessary to try to get rid of a property (discernibility) which no longer plays any role in the problem—the second procedure is a clear illustration of this fact).

The physical sense of the first procedure (without the superfluous step) is transparent. When $M \to \infty$, $N \to \infty$, $N/V = \text{const}$, the property of discernibility of the different ψ_i becomes "fine grained" enough to make the introduction of a thermodynamical meaning in the mixing entropy of ideal gases possible. The corresponding procedure is well known and is described, e.g., in Chapter V of the cited book of von Neumann. Namely, one has to find the extremum of S_M under the additional conditions $\Sigma_i p_i = 1$, $\langle E \rangle = \text{const}$, where $\langle E \rangle$ is the fixed average energy of the N-body system. After a corresponding variation one obtains

$$p_i = e^{-\beta E_i} / \sum_{k=1}^{\infty} e^{-\beta E_k} \tag{2.4}$$

where β is the "modulus" of the thermostat. Interpreting β as $1/k_B T$ we obtain the information entropy S of the canonical ensemble by replacing p_i in equation (2.2) with the expression (2.4) in which β has the above value. This entropy is identified with the thermodynamical entropy of our system since it is maximum in a state of equilibrium with the thermostat, the equilibrium values of p_i being given by equation (2.4) and, besides, it possesses all the typical properties of entropy [e.g., $S = -\partial F/\partial T$, the Helmholz function F being calculated using (2.4) too and so on]. This entropy will coincide also with that of the microcanonical ensembles when $N \to \infty$ owing to the already mentioned equivalence of the statistical ensembles in this case. In such a way we obtain the chain of equalities $S = S(N, V, T) = S(\langle E \rangle, N, V)$ where $S(N, V, T)$ is the entropy calculated with the help of the canonical ensemble and $S(\langle E \rangle, N, V)$—the entropy of the microcanonical one for $E = \langle E \rangle$.

In the general case the entropy S [equation (2.2)] does not have any thermodynamical meaning, and in the extreme case of an ensemble of systems in the same stationary state ψ_i, S_M gives "zero information" about the thermodynamical properties of ψ_i (let us remind the reader once again that only several statistical ensembles have a bearing on thermodynamics). In such a way the seeming contradiction is solved and the expressions (2.1) and (2.2) have obtained an interpretation acceptable from the point of view of physics: S_M [equation (2.1)] gives sensible information about the thermodynamical entropy of a many-body system only in a few cases of statistical ensembles. In the case when all the members of the ensemble are in a fixed state ψ_i, S_M gives no information whatsoever about thermodynamical entropy. This fact has certainly no relevance to the actual thermodynamical properties of a pure stationary state.

We can ascribe now definite thermodynamical properties, e.g., entropy S_{ψ_i}, to any stationary state ψ_i without being afraid that a contradictory situation may appear. Really, the above considerations mean that $\psi_i = \psi_{E,N,V}$ ($\psi_{E,N,V}$ is a brief notation of the fact that our N-particle system is closed in a volume V and is in a state of definite energy E) is an eigenfunction not only of the Hamiltonian H but of the entropy operator

$\hat{S}(H)$ too corresponding to an eigenvalue $S(E, N, V)$. This value, as the postulate says, can be obtained, at least in principle, from equation (2.2) in the case of a microcanonical ensemble. The entropy operator can be defined in a well-known way which is described for the general case in von Neumann (1932), Chapter II:

$$\hat{S}(H)=\int_{-\infty}^{\infty} S(\lambda, N, V)\, d\hat{E}(\lambda) \tag{2.5}$$

where $\hat{E}(\lambda)$ is the projection operator on the subspace formed by the eigenfunctions of H corresponding to energies $E \leqslant \lambda$. This operator, obviously, is defined in such a way that it gives the entropy $S_{\psi_{E,N,V}}$ of a state of energy E and, at the same time, the entropy S of the microcanonical ensemble constructed over states ψ_i of energy $E_i \in (E, E+\Delta E)$:

$$\begin{aligned} S_{\psi_{E,N,V}} &= \langle \psi_{E,N,V} | \hat{S} | \psi_{E,N,V} \rangle \\ &\approx \sum_{E_i=E}^{E+\Delta} p_i \langle \psi_{E_i,N,V} | \hat{S} | \psi_{E_i,N,V} \rangle \end{aligned} \tag{2.6}$$

(The entropy S is a continuous function of E according to phenomenological thermodynamics and the microcanonical ensemble is postulated to ensure this property.)

One can define analogically the temperature operator $\hat{T}$:

$$\hat{T}(H)=\int_{-\infty}^{\infty}\left[\frac{\partial S}{\partial \lambda}(\lambda, N, V)\right]^{-1} d\hat{E}(\lambda) \tag{2.7}$$

having a definite value $[\partial S(E, N, V)/\partial E]^{-1}$ in any state $\psi_{E,N,V}$ and so on. In such a way we can construct a complete set of operators which are applicable not only to the usual statistical ensembles but to all eigenfunctions of H as well, thus making a physically reasonable equivalence of statistical ensembles and the said functions possible.

The ease with which we came to the conclusion about such an equivalence is due to the discreteness (which leads to enumerability) of the stationary quantum states and the very concept of such a state. This fact made the above procedure of reversible separation of gases possible since they thus possess a clear-cut property, making them distinguishable. The proof of a similar theorem—the (quasi)ergodic hypothesis—for classical states of many-body systems has not been carried out yet for the general case owing to the complications arising from the classical concept of a state of motion: We have in this case an innumerable sequence of states of constant E defined by the positions of a representative point in the $6N$-dimensional phase space of the system. This is an essentially time-dependent situation and one is forced to seek a troublesome proof of the equivalence of ensemble- and time averaging. The concept of a quantum stationary state is quite different. It is much more akin to the concept of a classical microcanonical ensemble than to a classical state of motion since it does not depend essentially on time ($\psi_E(q,t)=\psi_E(q)\exp[-iEt/\hbar]$, so that a striking similarity between quantum and thermodynamical stationary states exists. Combined with the above said enumerability of states, this fact quickly leads to a physically clear result.

3. ON THE INCREASE OF ENTROPY WITH TIME

Equation (2.5) gives a general definition of the entropy operator $\hat{S}$ and it can be applied to nonstationary states as well like any other operator in quantum mechanics. We can show now that the usual prescriptions of quantum mechanics cannot make possible a prevalent increase of the entropy (2.5) with time. Indeed, let us examine the following typical irreversible process. An N-particle system is in a stationary state ψ_{E,N,V_1} and in moment $t=0$ its volume is increased suddenly (in a sense discussed in T1) to $V_2>V_1$. The well-known conventional prescription gives

$$\psi(t)_{t>0}=\sum_n a_{E_n,N,V_2}e^{-(i/\hbar)E_nt}\psi_{E_n,N,V_2} \tag{3.1}$$

where a_{E_n,N,V_2} are constants, $\Sigma_n|a_{E_n,N,V_2}|^2=1$. Consequently,

$$\langle S(t)\rangle_{t>0}=\int\psi^*(t)\hat{S}\psi(t)\,dq=\sum_n|a_{E_n,N,V_2}|^2S(E_n,N,V_2)=\langle S(0)\rangle \tag{3.2}$$

q denoting all the degrees of freedom of the system. The average value $\langle S(t)\rangle$ thus remains constant with time. It is obvious that this inference remains unaltered even when one takes a microcanonical ensemble of states $\psi_i\in(E,E+\Delta E)$ and performs the same act of an instantaneous increase of all identical volumes in moment $t=0$ since the entropies of the different ψ_i are practically equal and no one state changes its entropy according to (3.2). Therefore, no tendency of irreversibility can exist in the Schrödinger equation which is symmetrical to time reversal.

In order to make this fact even more vivid we shall examine a one-dimensional potential well of length a with impenetrable walls: $U(x)$

$=0$ for $0<x<a$, $U(x)=\infty$ for $x\leqslant 0$, $x\geqslant a$. One dimensionality is chosen for the sake of simplicity, everything remaining true for a rectangular three-dimensional potential well with a removable wall. Let our well contain N noninteracting identical particles of mass m in some overall stationary state ψ_i. The possible energies of the stationary states of the individual particles are equal to $E_{(n)}=n^2\pi^2\hbar^2/2ma^2$, $n=1,2,\dots$. The length of the well is increased instantaneously from a to b in some moment $t=0$. Equation (3.1) in which E_n are in our case the eigenenergies of the N-body system of "free" particles in the well of length b gives immediately that the initial form of the wave function $\psi(t)_{t>0}$ will be exactly restored in moments of time $t_k=4kmb/\pi\hbar$, $k=1,2,\dots$ (it is sufficient, obviously, to examine the behavior of a single particle in the said well since the initial state of the N-body system is a linear combination of products of individual eigenfunctions and any one individual state has the above property). In such a way the particles will collect periodically in the initial interval of length a, the finite period being $T=4mb/\pi\hbar$, according to the Schrödinger equation (for a subsystem of a larger system). We do not have thus an irreversible expansion in the above process in the conventional way of action. Clearly, the same remains true when one examines the above process applied to a microcanonical ensemble of eigenstates of the many-body system.

The discussion in T1 makes it possible to obtain an increase of S with time in a straightforward way. Indeed, consider a system of interacting particles in a volume V_1 which is large enough (or the density being large enough) to make the influence of the walls on the motion of practically all the particles negligible (with the exception of a small number of particles in the vicinity of the walls). The volume V_1 is then suddenly increased to V_2. When the overall system is in a state of (practically) definite energy, the subsystem consisting of our N particles will relax to a state of definite energy E_f too (cf. T1). Owing to the fact that only a vanishingly small part of the particles will "feel" the motion of the wall one is justified to expect that E_f will be practically equal to the initial energy E_i of the N-body system: $E_f\approx E_i$. The increase of S in this process follows immediately from our previous discussion and the first law of thermodynamics. Really, the variation ΔS of S in this process is equal to

$$\Delta S=\int_{V_1}^{V_2}\frac{\partial}{\partial V}S(E,N,V)\,dV>0 \tag{3.3}$$

since $\partial S/\partial V>0$ owing to the said law

$$dE=TdS-PdV \tag{3.4}$$

Really, when $dE=0$ we shall have

$$\frac{\partial}{\partial V}S(E,N,V)=\frac{P}{T}>0 \tag{3.5}$$

since the pressure P is always positive (the microcanonical ensemble is postulated to guarantee this property). The integration in (3.3) is lawful because, according to our discussion, any eigenstate of energy E of our N particles in a volume V has a definite entropy $S(E,N,V)$ and one has to calculate $S(E_f \approx E_i, N, V_2)$ starting from $S(E_i, N, V_1)$. This is certainly done with the help of the integration in (3.3). Consequently, despite the fact that the general evolution equation is yet unknown, its very existence makes it possible to obtain a numerical expression for the total increase ΔS of entropy in a typical nonstationary process. A more detailed information about the evolution can be obtained only if the exact equation is solved.

The same argumentation does away with the paradoxical periodical behavior of the system of free particles in the potential well. Indeed, this system will come irreversibly to a stationary state too and no behavior of such a sort is implied in a stationary state.

Up to this moment we had in mind N-body systems consisting of identical particles owing to the simplicity of the case. But everything said remains true for arbitrary many-body systems despite the fact that things do not seem so obvious then. We shall show that this is really so in the general case, clarifying in the way the physical sense of our definition (2.5) of entropy.

Consider, e.g., a system consisting of two types of interacting particles which are initially separated and let the separating wall disappear in moment $t=0$. According to the discussion in T1 the system will quickly relax to a state of (practically) definite energy E_n, the characteristic time of this process being determined by the relation $\Delta\mathfrak{E}\Delta t \sim h$. (Having in mind the possible dependence of $|a_n(t)|$ on t, considered in T1, one can easily see that we shall have first a relaxation to some group of almost degenerated levels, the state of strictly definite E_n being reached only in the limit $t \to \infty$). Owing to the thermodynamical equivalence of the stationary states ψ_i inside $(E, E+\Delta E)$, which is true in the general case, it is enough to come to a situation in which practically all members of the wave packet correspond to eigenenergies $E_i \in (E, E+\Delta E)$, $\Delta E/E \ll 1$. We can assert then that the entropy S has reached its value defined in equation (2.6). In this point the following problem appears: The above time-energy "uncertainty relation" gives a very fast relaxation of the initial state to a linear combination of the said group of ψ_i. We come thus to a definite S much earlier than the moment by which the ordinary diffusion of the different gases is essentially completed. But the process of diffusion is irreversible while we state that our entropy has reached its normal value prior to the end of this process.

The contradiction, however, is only apparent. An additional consideration of our S does away with it.

According to our discussion the purely stationary quantum states ψ_i with $E_i \in (E, E+\Delta E)$, $\Delta E/E \ll 1$, $N \to \infty$, are equivalent from the point of view of thermodynamics, so we can ascribe to them the same functions S, T, and so on. On the other hand, these ψ_i may have essentially nonequilibrium inherent properties as implied by the interpretation of $|\psi_i|^2$ as the coordinate probability density. Indeed, gigantic coordinate fluctuations from the most probable distribution can exist in a stationary ψ_i (e.g., a practically complete separation of the different components of the initially uniform mixture of gases) since $|\psi_i|^2 \neq 0$ in such cases also. In the conventional variant of quantum mechanics we do not know how to describe the evolution of such a fluctuation in a strictly stationary state ψ_i since ψ_i is written in a static notation ($\psi_i(x)\exp[-iE_i t/\hbar)$.

Allowing for the possibility of fluctuations (even gigantic ones) S has to be in fact an expression of some prevalent "average stability" only of ψ_i. This property will be practically identical for all $\psi_i \in (E, E+\Delta E)$. After the said fast initial reduction of ψ to a wave packet $\Sigma_i a_i(t)\psi_i$ where practically all $\psi_i \in (E, E+\Delta E)$ and $\Sigma_i |a_i|^2 = 1$ we come to a linear combination of physically indistinguishable states $[\langle\psi_i|\hat{S}|\psi_i\rangle \approx \langle\psi_k|\hat{S}|\psi_k\rangle;\ E_i,\ E_k \in (E, E+\Delta E)]$ which has to describe a situation, as empirical facts show, in which the process of diffusion has not yet practically begun. Owing to the physical indistinguishability of the said ψ_i we can now treat the above wave packet as a gigantic coordinate fluctuation in some stationary state. The gradual disappearing of all $a_i(t)$ with the exception of a fixed $a_n(t)$ (we know that we have to come to a definite stationary state ψ_n when $t \to \infty$) will cause the disappearing of the fluctuation in the process of its evolution. Consequently, we have obtained the possibility of considering intimate inner properties of the stationary states ψ_i due to the above definition and interpretation of entropy of a pure state.

The reader has probably noticed the complete parallelism between our interpretation of the wave packets of thermodynamically (practically) indistinguishable states and the interpretation of "usual" wave packets composed of eigenstates ψ_α corresponding to a quasiclassical motion. In the latter case a fixed $\psi_\alpha(q)$ does not give a dynamical picture of the motion of the particle as well but a linear combination of $\psi_\alpha(q)\exp[-iE_\alpha t/\hbar]$ with slightly varying values of the set of parameters α can provide (for a certain period of time) a picture corresponding to our classical concepts of motion. One can certainly ascribe this picture to practically any one of the stationary states of which the packet is composed. In an analogical way we interpret the thermodynamical wave packet as a dynamical picture of the internal properties of a stationary state. In both cases the wave packets will be comparatively slowly reduced to fixed eigenstates according to the general discussion in T1.

Consequently, the irreversible master equation will describe two different things:

(1) It will give information about the interval of time during which the system of interest will pass from a highly unstable initial state to a state ψ which can be interpreted as a gigantic fluctuation of a stationary $\psi_n \in (E, E+\Delta E)$. Because of this we can say that we have come to a definite property S which characterizes an overwhelming tendency of such a ψ_n. In our specific example this will be a tendency to the most probable coordinate distribution of the system in a state of motion ψ_n; this tendency is a direct consequence of the internal physical properties which uniquely determine all the thermodynamical properties of the manybody system. $\langle \psi_n | \hat{S} | \psi_n \rangle$ is a "measure" of this tendency. It does not depend on time—a purely ergodic property.

(2) The master equation will then give the actual realization of the said tendency by describing the gradual disappearing of the gigantic fluctuation in the process of mixing of the gases; this can be characterized by some relevant information entropy if necessary.

The above inference is general. The specific case examined is only an illustration of a typical way of reasoning.

The assertion that S is a continuous function of E (for fixed N and V) is not true only for points in which phase transitions take place. This is inessential since the considerations apply to intervals $(E, E+\Delta E)$ which do not contain the transition points.

We pointed out in the beginning that any approach to irreversibility based on the time-reversible conventional equations is inevitably connected with the postulation of hypotheses which do not follow from the basic theory. We shall illustrate this briefly with a few examples.

The first attempt for a proof of the H theorem in the orthodox variant of quantum mechanics without molecular chaos-type assumptions, as it is declared, belongs to von Neumann (1929). However, his theory of macroscopic measurements and the introduction of a "virtual" microcanonical ensemble U_ψ based on this theory, the entropy $S(U_\psi)$ of which corresponds to the entropy $S(\psi)$ of a single state, is in fact an assumption of exactly such a type [$S(\psi)$ is also based on the theory of macroscopic measurements and has no bearing to S_ψ in our previous discussion]. Indeed, this manipulation is analogical to the usual introduction of coarse-grained distributions. Another assumption shows that von Neumann examines in fact a model of a rather contradictory character. Namely, it is presumed that the procedure of macroscopic measurement of energy is so rough that only large groups of levels are discernible and, at the same time, so fine that it is possible to determine the exact boundary between any pair of such large groups. And lastly, von Neumann himself states in his introduction that owing to symmetry of the *SE* with respect to time reversal one cannot prove the H theorem in the ordinary form $S(t_1) \geqslant S(t_2)$ for $t_1 \geqslant t_2$. This statement is quite convincingly supported by the fact that von Neumann uses a wrong sign before the time derivative $\partial\psi/\partial t$ (he works in fact with the equation $-ih(\partial\psi/\partial t) = H\psi$ but this is inessential for his approach). What von Neumann shows in his model is that the time average of $S(U_{\psi_t}) - S(\psi_t)$ has to be a small quantity if a number of quite strong additional assumptions are made (one of which is the nondegeneracy of the eigenstates of the many-body system). One cannot thus think seriously that the problem has been solved in this work or, at least, that it has obtained a clear formulation.

Two recent definitions of quantities which have the property to increase with time and are postulated to be the entropies of the corresponding systems can be found in the works of Zubarev (1971) and Prigogine et al. (1973). It is shown in Appendix III of the former work that a time-irreversible conduct can be obtained with the help of the introduction of an infinitesimal "source" into the Liouville equation for the quantum statistical operator ρ:

$$\frac{\partial\rho\hat{\varepsilon}}{\partial t} + \frac{1}{ih}[\rho_\varepsilon, H] = -\varepsilon f(\rho_\varepsilon) \tag{3.6}$$

where $f(\rho_\varepsilon)$ is a function of $\rho_\varepsilon(t)$. The source $-\varepsilon f(\rho_\varepsilon)$ breaks the symmetry with respect to time reversal and $\lim_{\varepsilon \to +0} \rho_\varepsilon(t)$ is supposed to be the correct statistical operator. In the work of Prigogine et al. a similar step exists. It consists of a contour integration in the upper half-plane. This is the first step in a series of manipulations which lead to a quantity increasing with time.

It is hard to say that the above two approaches have a transparent physical meaning (leaving aside the problem of mathematical rigor). Our previous discussion shows that the ordinary mechanism of quantum theory cannot guarantee an increase of entropy if one starts from the definition (2.5) of the entropy operator. Quite probably, the system of axioms of the conventional theory is essentially broken in the above methods. It is worth pointing out in this context the similarity between the introduction of sources into the Liouville equation and the introduction of a term $\hat{\Gamma}\psi$ in the Schrödinger equation in T1, both operations ensuring time irreversibility. The fact that the introduction of infinitesimal terms in the Schrödinger equation is by no means an innocent action when very large time intervals are considered can be seen in the detailed discussion in our forthcoming paper (Todorov, to be published; hereafter referred to as T4).

4. CONCLUSION

The present work does not claim to have solved the difficulties in statistical mechanics. The approach to the problem of entropy increase outlined above may encounter serious impediments in a future theory (which we hope to exist) from the point of view of a rigorous practicable realization. But we believe that our considerations provide a sound basis for the formulation and consideration *in principle* of some problems in statistical physics.

Our attention was concentrated chiefly on the physical aspects of the problem since it can turn out that the hope of an actual mathematical rigor in the N-body problem is illusory. One is forced to make a number of assumptions based on physical intuition even in works which are declared to be mathematically rigorous.

According to the ideology of our paper T1 developed further in the present work the (thermodynamical) properties of a system of particles are determined solely by the inherent physical nature of the said system. Measurements and other extraneous effects are not supposed to play an essential role (certainly, as long as no noticeable exchange of energy between our system and extraneous systems exists). This is in marked contrast to generally accepted notions—compare, e.g., with the ideology of von Neumann (1929, 1932). Our work T4 contains a further development of the said concept.

In the paper of Ta-You Wu (1975) it is shown that one has to go beyond classical mechanics in order to prove Bolzmann's H theorem. In this work we show further that one has to go beyond conventional quantum mechanics for an honest treatment of irreversibility. More exactly, the postulate (I) in T1, which is basic for orthodox theory, has to be abandoned in the general case.

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