

||
R. C. Archibald

Th 56895
La. 6-8139

Ia

On the Entropy in Quantum theory.

Stashevski To gain a better understanding
of the thermodynamical meaning of ~~a Lemann's~~
~~expression for the entropy of a system in quantum~~.
theory ^{by writing} introducing the conception of ^{the} m-entropy, ~~is intro-~~
~~which is~~ the minimum increase in entropy of the
measuring apparatus produced by the measurement (Gzilard).

Ib
the Entropy in)

In Quantum Theory and Thermodynamics

The following considerations are an attempt to get a better insight into the connection between quantum theory and thermodynamics.

So far the main work on this problem has been done by v. Neumann. He derived a general expression for the entropy of a system in quantum theory:

$$S = -k \sum \omega_i \ln \omega_i \quad (k \text{ Boltzmann Konstant})$$

where The system is considered as a mixture of pure cases, and the ω_i are the weights of the pure cases in the mixture and the entropy of a pure case is $\neq 0$.

The so defined entropy has a statistical meaning but is in general not a thermodynamical entropy. In thermodynamics the entropy difference ΔS between two states A and B of a system is defined by

$$\Delta S = \int dQ^A / T_A + \int dQ^B / T_B$$

where dQ^A is the amount of heat given to the system at the temperature T in a reversible process. v. Neumann showed that his definition of the entropy of a system is identical with the thermodynamic one for a mixture of stationary energy states in equilibrium. He made it plausible that

Such a system is certainly not in thermodynamical equilibrium with the surroundings. Of course, it is possible to give a definite meaning to ^{the entropy of} non-equilibrium states. In fact it is necessary to do so for many applications of thermodynamics. However, to talk of the entropy of a mixture of pure states where a state may be a particle with extend this procedure to all quantum states - a pure state ^{may be} of a free particle with $A_p A_q = \frac{\hbar}{4\pi c}$ - seems artificial. Therefore it seems to me desirable to find out clearly the thermodynamical meaning.

The state of a system in quantum theory is defined as a result of measurements. By ~~extending~~^{using} an idea of Szilard we use the conception increase in entropy of the measuring apparatus. We call it m-entropy. Szilard proved that for a measurement deciding which one of two possibilities is realized, ~~with~~^(The increase of entropy is at least $k \ln 2$) Following the method of Szilard we have first ~~to~~^{This is for} determine the m-entropy for a classical system, which is similar to a system in quantum theory as it has a finite number of states, calculate the m-entropy for the determination of ~~the~~^(the) configuration of atoms in a solid solution.

~~It is an assumption that is have definite value for every measurement.~~

For statistical purposes it is a sensible generalisation to admit as pure states not only stationary energy states but any kind of pure quantum states e.g. a particle with known position and impulse known within the limits of Heisenberg's uncertainty relation.

It seems to me that one can give v. Neumann's entropy also a thermodynamical meaning ^{by elaborating on idea of Szilard introducing the conception of m-entropy of a measurement} and ~~and defining~~ representing the minimum increase in entropy produced in the measuring apparatus if one changes by measurements the system to a pure case whose entropy is zero. I shall call it entropy the m-entropy. That is a continuation of the work of Szilard who proved that $k \ln 2$ is the minimum amount of increase in entropy if one determines by measurement which one of two possibilities is realized.

First I want to show the difference between the thermodynamic entropy and the m-entropy on a simple classical example discuss the m-entropy with a classical example, a solid solution, or rather the is especially suited (to our purpose) for the following reasons. Generally there is no zero point for the entropy in classical part of the entropy due to the configuration of the atoms.

III)

11. case: For one mol of the solid solution.

the systematical term in the entropy is

$$-R \sum x_i \ln x_i \quad (R \text{ gas constant}, x_i \text{ Mol-fraction of the } i\text{-th component})$$

$$= S_m - \sum x_i S_i = \Delta S \quad S_i \text{ its entropy in the pure state, } S_m \text{ entropy of the mixture}$$

It is the increase in entropy ~~when we mix the~~
~~we disregard for the moment they~~
 components, plus other terms which ~~are very small~~
 when the components are similar, e.g. isotopes). This
 last assumption is not essential for the following.

At high temperature with ~~nowhere~~ diffusion takes place

We can measure ΔS by reversible mixing (by distillation).

At lower temperature we could, ^{now} in principle, make the following experiment: The solid mixture will in the course of time assume all possible configurations.

The probability for every configuration (or the fraction of time during which this configuration is realized) is essentially proportional to $e^{-E_i/kT}$

(E_i energy of the i -th configuration, T absolute temperature).

We assume first $kT \gg E_i$ for all configurations. ^{they are all equally probable.}

Then we wait till the configuration is realized

where the components are unmixed. In this moment we separate the components and mix them again

in a reversible way. By this process we withdraw from the surroundings (temperature bath) the entropy

$-k \sum x_i \ln x_i$. In order to avoid a contradiction to the second

Therefore we ~~can~~ conclude from

V)

~~as we can see from~~
 You cannot prove it but make it plausible by
 as the following argument. We start at the high temperature T_1 ,
 (with the solution) we don't know the configuration and cool it
 down to T_2 (the low temperature), fast enough not to change the unknown
 The $\Delta S = \int_{T_1}^{T_2} \frac{C}{T} dT$, where C is the difference
 of the specific heats of the mixture and the pure
 components. The specific heat of the mixture
 can be considered as composed of the
 two parts, one part representing the change of the
 vibrational energy of the atoms with the configuration fixed,
 the second part originating from the change
 of configuration and contributing to C because of the
 energy differences of the different configurations. It is
 the latter part which ^{is responsible for} changes the systematical term

$-R \sum x_i \ln x_i$. If we now we measure the configuration
^{in this case only} ~~of the solution~~ ^{of the solution} the cooling is strictly not reversible.

If we know all pure state otherwise mixture, with weights w_i .

Then $S = -k \sum w_i \ln w_i$. Now entropy $S = \frac{\partial Q}{T}$ equilibrium. That
 shows directly that q th ^{in general} ~~state~~ ^{pure} state stationary
 energy state. All other ^{pure} states e.g. $\Delta p \Delta q = \frac{\hbar}{2\pi}$ - can be considered
 as superposition of energy states. But the coherence will be destroyed

~~not equil. in temp. equilibrium~~, so the q entropy cannot be the therm. entropy.
~~state statis.~~ Since connected with measurement ^{would prefer to} ~~it~~ shall call it the m -entropy

^{xx} for a detailed calculation J. Henr. Ann. d. Phys.

at the low temperature T_1 , bring
 without change in the configuration,^{which cancels S_0 at cooling}
 the high temperature T_2 , in a reversible way the crown con-
 figuration into the solution. Thereby we diminish the
 entropy of the surroundings by the amount $-R\sum x_i \ln x_i$, that
 means that the measurement at low temperature must have
 increased the entropy by at least the same amount. The
 assumption that we can arbitrarily prevent a change in
 configuration corresponds to the assumption of a 'negative'
 catalyst made in the thermodynamical derivation of the
 laws of chemical equilibrium. The value $-R\sum x_i \ln x_i$ is
 of course only the average value if we repeat the
 measurement many times, as is the case with all quan-
 tities in statistical thermodynamics because of the Brownian
 fluctuations.

B. VI a

Now to v. Neumann's definition of entropy as follows.
 Representing the state of the system by a Gibbs ensemble
 he defines it by a statistical matrix P in the following way.
 First for a pure case. The η -function in this case can
 be considered as a superposition of energy states:

$$\Psi = \sum_n c_n(t) u_n(\eta), \quad c_n = a_n e^{i\omega_n t} e^{-i\frac{E_n}{k} t}$$

where a_n is real, ω_n a phase constant and the other letters have the usual meaning.

^{1/4} following essentially the representation by W. Pauli, Handbuch der Physik XXIV, p. 149,
 Berlin 1933

VI d

The m-entropy has a well defined meaning also in the case of a measurement on a quantum mechanical system. As Bohr often emphasized, the measuring apparatus is always to be considered as classical. Therefore the m-entropy is a change of the ordinary thermodynamic entropy of a classical system ^{as a function of state of the macroscopic variables}. Representing the quantum system by a Gibbs ensemble of independent systems we have to carry ^{out} the measurement ^{on a large number of systems} and the m-entropy ~~for the system~~ in the following is understood as the average for the N measurements.

~~We can include that von Neumann's expression for the entropy of a mixture is nothing else as the m-entropy for the measurement whose result ~~is~~ the pure cases which form the components of the mixture by considering his derivation.~~

The expression $-k \sum c_i \ln c_i$ for the entropy of a mixture can be considered as the m-entropy.

We can see from a discussion of von Neumann's derivation,

VIIa

First he characterizes a system by its statistical
that is

$$P = \sum_i \omega_i P_i \quad (\omega_i \geq 0, \sum \omega_i = 1)$$

where the P_i are matrices of pure cases which
are defined as follows. The ψ -function of a pure case
is considered as a superposition of energy states:

$$\psi = \sum_n c_n(t) \psi_n(q), \quad c_n(t) = a_n e^{i\alpha} e^{iE_n t} \quad (\alpha \text{ real, } a \text{ phase constant}),$$

then

$$P_{m,n} = C_m^*(t) C_n(t)$$

and the average for a physical quantity with the
operator F is: $\bar{F} = \sum_n (FP)_{nn}$

for the pure case as well as for the mixture.

~~For the pure case is phase connection between
The same energy states can form a pure case by
superposition or a mixture with no phase connections
between the components.~~

* W Pauli, R. (S. VI)

~~Then P is defined by~~

$$P_{m,n} = C_m^*(t) C_n(t)$$

~~and the average of any operator F is~~

$$\mathcal{F} = \int y^* F y dq = \sum_m (\mathcal{F} P)_{m,n} \quad F_{mn} = \int u_n^* F u_m dq$$

~~If we don't know all we can know about the system it has to be considered as a mixture of pure cases with the statistical matrix.~~

$$P = \sum \omega_n P_n \quad (\omega \geq 0, \sum \omega_n = 1)$$

~~where the parameters of pure cases. Then formula remains valid. For the pure case one $\omega = 1$, all others zero.~~

~~The main point is that in a pure case considered as a superposition of other states - also pure cases - the components interfere in the mixture they don't.~~

~~To take a simple example. We consider an atom in two energy states, the ground state and the next higher one. If the last one is excited by resonance radiation we have a pure case, if it is excited by temperature we have a mixture. In both cases we have two energy states but if we calculate e.g. \bar{q} we get~~

~~for the pure case: $\bar{q} = a_1^2 q_1 + a_2^2 q_2 + 2a_1 a_2 q_1 \cos(\nu T + \alpha)$~~

$$\hbar\nu = E_1 - E_2, \alpha = \alpha_1 - \alpha_2, \omega_0 = 1 \text{ all others zero } S = \hbar |ln| = 0$$

~~for the mixture: $q = a_1^2 q_1 + a_2^2 q_2, \omega_1 = a_1^2, \omega_2 = a_2^2, S = \hbar(\omega_1 \ln \omega_1 + \omega_2 \ln \omega_2)$~~

$$\omega_1 + \omega_2 = 1$$

To derive his formula v. Neumann proceeds in the following manner.

~~v. Neumann's~~ That expression for the entropy $S = k \sum w_i \ln w_i$ is nothing else as the m-entropy follows directly from his derivation. He encloses every member of the ensemble representing the system in a box and considers the boxes as molecules of an ideal gas in ~~Temp.~~ equilibrium. Then he introduces semipermeable walls, every one of these permeable for ~~one~~ pure state component of the mixture but impermeable for the others. In this way ~~only~~ ^{can it be reversible} separate ~~the mixture state into the component pure states of the mixture.~~ This separation is ~~also affected really done~~ ^{the} ~~do the same~~ by measurements which result in the pure states. So v. Neumann's procedure ^{should} be considered as an artifice to determine the minimum increase in entropy produced by ~~the~~ measurements in the surroundings which must be at least equal to the entropy of the mixture of ideal gases (box-molecules).

To exemplify with the simple case of ^{again} two energy states:

We can separate them by a molecular ray experiment using ^{eq.} an inhomogeneous electric field if the polarisability of the two states is different. To determine the minimum increase of entropy in such an experiment ^{on the other hand} would be certainly possible but difficult. ~~but of we~~

IX

have ^{a mixture of} atoms of two different elements we know that the minimum increase in entropy required to separate them by any method is $-k \sum_{i=1}^n n_i \ln n_i$ ^{therefore} also for the mol-ray experiment. Since the experiments (it makes no difference if we have two different elements or two energy states ^{of the same element}) we can assume that in both cases the m-entropy is $-k \sum_{i=1}^n n_i \ln n_i$.

Furthermore since ^{experimentally} it makes no difference if the excited state is produced by resonance radiation ^{or} temperature, it is natural to assume that the m-entropy is the same in both cases. This result is apparently connected with the fact that the classical measuring apparatus necessarily destroys the phase-connections (Bohr).

Therefore I assume that it has general validity, and for the m-entropy it makes no difference if the states resulting from ^{the} measurements were components of a pure state (phase-connection) or of a mixture. To find the m-entropy for measurements on a pure state resulting in other pure states ^{one has to proceed as follows} in other words: On represents the original pure state ^{as} a superposition of the pure

^{On this point} I want to acknowledge several helpful discussions I had with P. in Dec 1946. ^{on the minimum increase in entropy for measurement on a pure case.}

This became clear to me first after several discussions with V. Pauli in Dec 1946 to whom I submitted the problem what the min increase of entropy is if one measures ^{one pure state}

X

states y_i resulting from the measurement

with $y = \sum c_i y_i$,
 then $|c_i|^2$ is the probability of finding the state y_i ,

and $-k \sum c_i \ln c_i$ is the m-entropy of our measurement.

~~It depends of course on the variable which we measure.~~

Only for the measurement which defines the pure state the m-entropy is zero.

~~to derive the quantum laws)~~

~~It should be possible by reversing the argument,
 defining the pure state as one for a special measurement
 for which the m-entropy is zero and replacing the superposition principle
 by the assumption that for other measurements the m-entropy
 is $-k \sum c_i \ln c_i$. With the addition of the uncertainty principle
 or some equivalent principle.~~

Q { I am hoping that looking at the quantum theory
 from the thermodynamical viewpoint might give us ~~the preceding considerations are~~ ~~any theory~~
 a better physical understanding ~~of quantum mechanics and its~~ ~~first step~~
~~to progress in the solution of some problems.~~

~~where c_i are the probabilities of getting the other pure states resulting from the measurement, in connection~~

~~& that a measurement on a pure state giving a result other pure states requires a finite amount of entropy, that is the exact meaning of the statement, that the measurement in quantum theory is an irreversible process.~~

The reason for the irreversibility of measurements on a pure state are irreversible - except for the measurement which defines the pure state - because they require necessarily a finite m-entropy, not because they result in a mixture, which they don't necessarily.

Measurements on a mixture are reversible, in principle, if they result in the pure states composing the mixture. If other states result from our measurements where others states result than the measurements are irreversible.

We could use these considerations to define a pure state as one for which for a specially the m-entropy is zero and call a system for which we can find measurements which result in pure states a mixture of these states. (Replacing the superposition principle) By our assumption about the m-entropy for measurements on a pure case one should be able, by using the uncertainty principle or some similar axiom, to give a thermodynamical derivation of the laws of quantum theory.

In this connection one has to consider
meaning of the ~~Pernst~~-theorem (third law) for the
m-entropy.

In thermodynamics we can formulate it so: We can withdraw from a system only a finite amount of entropy, though. In analogy we can say that also through measurement we can withdraw only a finite amount of entropy from a system, the m-entropy is always finite. In classical theory where we can measure as exactly as we want there are no limits for the m-entropy. For the statement that we can ^{not} reach the zeropoint of the absolute temperature, which means that we can ^{not} reach by cooling a state of a system with entropy exactly zero, the analogous statement is that we can't produce strictly a pure case for which the m-entropy is exactly zero. We can approximate it only asymptotically in the same way as we can approach zero temperature.

see X 9

