Postulational Basis of the Law of Increase of Entropy

(Gibbs–Tolman development/Boltzmann function/quantum mechanics)

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ABSTRACT The law of increase of entropy is shown to be a consequence of the central assumption, in the manner of Gibbs, for the construction of the ensemble that represents the physical system. It is no longer necessary to make two separate assumptions in the Gibbs–Tolman development of the bases of statistical mechanics.

I give a proof of the law of increase of entropy, from the Gibbs–Tolman viewpoint. What I have to say is brief and will look entirely trivial after it has been said, but it is apparently not in the large literature on the question. The law is usually justified in quantum statistical mechanics by the following argument:

- a. A kinetic equation is written for the time rate of change of the Boltzmann H -function (1). Time derivatives of statistical occupations are expressed in terms of the master equation.
- b. Application of the principle of detailed balance then leads to the result that in a closed system the H -function cannot increase with time (2, 3).
- c. The entropy can be identified as the negative of the H -function, whence the entropy of a closed system cannot decrease.

In place of the identification (c), the connection of thermodynamics with statistical mechanics follows in many respects more naturally when the entropy is defined as the logarithm of the number of quantum states accessible to a closed system.* Then the theory of equilibrium thermodynamics follows from a single essential assumption about the ensemble that represents the physical system: every stationary quantum state accessible to the actual system is represented in the ensemble by one closed system. This or some equivalent assumption can hardly be avoided.

The fundamental assumption contains and leads directly to the law of increase of entropy. We consider two closed systems with energies U_1 and U_2 , and entropies.

$$\sigma_1^0 = \log g_1(U_1); \quad \sigma_2^0 = \log g_2(U_2), \quad (1)$$

where g_1, g_2 are the numbers of accessible states. The total entropy of the separated systems is

$$\sigma^0 = \log g_1(U_1)g_2(U_2), \quad (2)$$

and I must show that the entropy increases or remains constant when the two systems are placed in thermal contact. Suppose the two systems are placed in weak interaction and exchange quanta of energy u_i . The total number of accessible

states is now, by reapplication of fundamental assumption,

$$\sum_i g_1(U_1 + u_i)g_2(U_2 - u_i), \quad (3)$$

with the sum taken over all possible values of u_i . The entropy σ of the combined systems is given by the logarithm of the sum (3).

Because (3) is a sum over positive terms, one of which is the initial entropy (2) for which $u = 0$, it follows that $\sigma > \sigma^0$, and the entropy increases because the two systems were brought into contact. It is important to observe that the entropy is increased significantly not because of the sheer number of terms† in (3), but because there will, in general‡, occur in the sum terms that are very, very much larger than the initial degeneracy $g_1(U_1)g_2(U_2)$. Let $\bar{u}$ be the most-probable value of the energy transfer when the systems are brought into thermal contact. For large systems, the entropy is given to an excellent approximation§ by the logarithm of this largest term in the sum, Eq. (3):

$$\sigma \cong \log g_1(U_1 + \bar{u}) + \log g_2(U_2 - \bar{u}). \quad (4)$$

It is of course (4), and not the exact expression

$$\sigma = \log \sum_i g_1(U_1 + u_i)g_2(U_2 - u_i), \quad (5)$$

that is additive when two systems at the same temperature are placed in thermal contact.

The model treated here is not lacking in generality in the contexts in which the result is required. The identical argument applies to particle exchange and volume exchange between two systems, and from the fundamental assumption alone it follows that the entropy increases when systems are combined that initially were at different temperatures, chemical potentials, or pressures. How does the argument apply to a single system? I view the “two systems” as two different sets of the quantum states of a single system, for example, states of even and odd parities. The entropy increases when a weak interaction that does not conserve parity is applied. Or one system may be a single state, and the other system all other states. No claim is made that this method bears or throws

† The number of terms alone has an effect on the entropy of the order $(\log N)/N$ and may usually be neglected.

‡ Except if the systems are initially at the same temperature, for then $\bar{u} = 0$.

§ This is the central statistical property of large systems. In our example it is enough if one of the two systems contains a large number of particles.

* A “state” is a stationary quantum state of an entire system.

light on the ergodic problems of mechanics, for I do not offer a proof of what is taken as the fundamental assumption¶. This argument is not dynamical, for the quantum states are

¶ Neither is it claimed that there is anything incorrect or inconsistent about the Boltzmann definition of the entropy. By proving that the alternate definition $\sigma = \log g$ has as a direct consequence the law of increase of entropy, I have removed perhaps the last strong motivation for viewing the Boltzmann identification as the basic definition.

stationary, and the entropy is defined here only for systems in statistical equilibrium. The sense of time enters only as the sequence in which the several operations are performed.

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2. Pauli, W., *Sommerfeld Festschrift* (Leipzig, 1928), p. 30.
3. Boltzmann, L., *Wien. Ber.*, **76**, 373 (1877).