

## THE DEFINITION OF ENTROPY IN NON-EQUILIBRIUM STATES

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### Synopsis

Several different expressions are used in statistical mechanics for the entropy. They are here evaluated explicitly for non-equilibrium states. The result consists of three terms: (i) the equilibrium entropy; (ii) the familiar quadratic term measuring the departure from equilibrium; (iii) a term referring to the fluctuations. Only the last term differs for the several expressions for the entropy. However, it is much smaller than the second term when the departure from equilibrium is large compared to the size of the fluctuations.

### 1. INTRODUCTION

In *thermodynamics of equilibrium states*, entropy is introduced as a well-defined state variable, i.e., a function of the *macroscopic* variables determining the macroscopic state of the system. In *non-equilibrium thermodynamics*, entropy is defined by decomposing the total system in subsystems, each of which is supposed to be in equilibrium, and adding their individual entropies. In this way one obtains for the thermodynamical entropy  $S_T$  near equilibrium <sup>1)</sup>

$$S_T = S_T^{eq} - \frac{1}{2} \sum_{ij} s_{ij} \alpha_i \alpha_j.$$

Here  $\alpha_i$  is used to denote the macroscopic variables measuring the departure from equilibrium, and  $s_{ij}$  is a constant positive-definite matrix. Of course, the accuracy with which a macroscopic quantity can be defined is limited by the existence of fluctuations. Accordingly the above definition is only physically meaningful provided one neglects certain small terms, which vanish if the number of particles tends to infinity.

*Statistical mechanics* has the task of providing an expression for the entropy in terms of the *microscopic* variables of the system. This microscopic entropy value must coincide with the macroscopic value, both in equilibrium and in non-equilibrium states, with a permissible error of the same order as the inaccuracy inherent in the macroscopic value of  $S_T$ . Three different expressions have been suggested, which I shall label with the names of Boltzmann, Fierz and Gibbs, and denote by  $S_B$ ,  $S_F$ , and  $S_G$  <sup>2)</sup>. It is well

known that in equilibrium these three expressions have the same value, apart from a small difference, which is completely negligible for a macroscopic observer. Our main purpose is to show that the same is true for non-equilibrium states. Hence the choice between the three expressions reduces to a question of convenience or elegance. In the last section some arguments are presented in favor of a modification of the Gibbs expression.

2. THE THREE EXPRESSIONS FOR THE ENTROPY

Consider a closed and isolated system, so that there is a well-defined set of canonical variables  $p_1 \dots q_1 \dots$ , and a time-independent Hamiltonian  $H(p, q)$ . Let there be a set of functions  $a_r = A^{(r)}(p, q)$  which are sufficiently slowly varying to make their time-dependence macroscopically observable. A set of values of the  $a_r$  can be represented by a point in "a-space". To each point  $(p, q)$  in phase space belongs one point in a-space; but to each point in a-space there belongs a many-dimensional manifold in phase space. A small cell  $\Delta a_1 \Delta a_2 \dots$  in a-space determines a macroscopically well-defined state of the system. On the other hand, it corresponds to a large domain in phase space, determined by

$$a_r < A^{(r)}(p, q) < a_r + \Delta a_r. \quad (r = 1, 2, \dots)$$

Let this domain be denoted by  $Z^*$ . Its phase volume must be proportional to the volume of the cell in a-space, so that a function  $G(a)$  may be defined by putting

$$\int_Z dp dq = G(a) \Delta a_1 \Delta a_2 \dots$$

*The Boltzmann entropy.* Boltzmann's relation between entropy and probability is in our notation

$$S_B(a) = k \log G(a).$$

More precisely: the microscopic state of a system is represented by a point  $(p, q)$  in phase space; to  $(p, q)$  there belongs a point  $a_r = A^{(r)}(p, q)$  in a-space and hence a value of  $G(a)$ ; the value of  $S_B$  associated with the microscopic state  $(p, q)$  is then defined by the above equation.

*The Fierz entropy.* As time proceeds,  $(p, q)$  moves in phase space according to the equations of motion, and the a-point moves along some curve in a-space. These curves have an extremely complicated zig-zag structure, and through each a-point passes an infinity of such curves. Since one is not interested in the detailed behavior of each curve, but rather in the over-all trend, one is led to the idea of treating the motion in a-space as a diffusion process. This amounts to introducing a probability distribution

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\*) In fact, it is a slight generalization of Ehrenfest's Z-star. Our formula defining  $G(a)$  assumes that the volume varies smoothly with the  $a_r$ , which in actual applications is always true.

$P(a, t)$  in  $a$ -space. The entropy is then taken to be the average of  $S_B$ :

$$S_F[P] = k \int P(a) \log G(a) da.$$

It should be noted that this is no longer a function in  $a$ -space, but rather a functional of the distribution  $P$ .

*The Gibbs entropy.* On the other hand, one knows from information theory<sup>3)</sup> that it is possible to construct a functional of the probability distribution which has all the properties one usually expects from the entropy<sup>\*</sup>). When applied to the present case this functional takes the form

$$S_G[P] = -k \int P(a) \log \frac{P(a)}{G(a)} da.$$

### 3. EQUILIBRIUM

Among the  $A^{(r)}$  there may be some macroscopic integrals of the motion, like the total energy. The other  $A^{(r)}$  describe the departure from equilibrium, and may be chosen such that they are zero at equilibrium. Without serious loss of generality we shall suppose that the energy is the only constant of the motion,  $A^{(0)}$ , and that there is just one other slowly varying macroscopic variable  $A^{(1)}$ . Then one has

$$G(a_0, a_1) = G(a_0, 0) e^{-\frac{1}{2}n(a_0)a_1^2}, \quad (1)$$

neglecting higher terms in the exponent.

According to the *Boltzmann point of view*,  $a_1$  is not exactly zero in the equilibrium state but fluctuates around this value. Hence also  $S_B$  fluctuates with

$$k \log G(a_0, 0)$$

as a maximum value. This value might be taken as the Boltzmann expression for the entropy of a system in equilibrium. It is more customary to use the integral over the whole surface of constant energy,

$$k \log \int G(a_0, a_1) da_1 = k \log G(a_0, 0) - \frac{1}{2}k \log (g/2\pi); \quad (2)$$

or even the total volume enclosed by it,

$$k \log \int_0^{a_0} da_0 \int G(a_0, a_1) da_1.$$

It is well-known that for large systems these three expressions are practically the same (Lorentz's "insensibilité de la formule de Boltzmann"<sup>5)</sup>). We shall take (2) as the Boltzmann entropy in equilibrium,  $S_B^{eq}$ .

<sup>\*</sup>) It should be emphasized that I merely quote a mathematical result obtained in information theory; I consider the point of view that information theory justifies the use of ensembles<sup>4)</sup> as a fallacy.

According to the *ensemble point of view*, equilibrium is described by a certain distribution,  $P^{eq}(a_0, a_1)$ . Since we are dealing with a fixed value,  $E$ , for the energy, we have to take the microcanonical distribution,

$$P^{eq}(a_0, a_1) = \frac{1}{\omega} G(E, a_1) \quad \text{for } E - \Delta E < a_0 < E,$$

$$= 0 \quad \text{for } a_0 < E - \Delta E \quad \text{or } a_0 > E.$$

Here  $\omega$  is a normalizing factor,

$$\omega = \Delta E \int G(E, a_1) da_1 = \sqrt{\frac{2\pi}{g(E)}} G(E, 0) \Delta E.$$

By substituting  $P^{eq}$  and using (1) one finds

$$S_F^{eq} = k \log G(E, 0) - \frac{1}{2}k \tag{3}$$

$$S_G^{eq} = k \log G(E, 0) - \frac{1}{2}k \log(g/2\pi) + k \log \Delta E. \tag{4}$$

Each of the three expressions (2), (3), (4) contains the term  $k \log G(E, 0)$ . This term is of order  $N$ , if the number  $N$  of degrees of freedom tends to infinity,  $E/N$  being kept constant. Hence the second term in  $S_F^{eq}$  is of relative order  $N^{-1}$ , and therefore negligible. The second term in (2), which also occurs in (4), is of order  $\log N$ , because  $g$  is the mean square fluctuation of  $a_1$ . The magnitude of the third term in (4) depends on the choice of  $\Delta E$ , the thickness of the energy shell. It is sufficient that  $\Delta E$  is smaller than the experimental inaccuracy in measurements of the total energy  $E$ , and in addition that the relative change of  $g(E)$  in the interval  $\Delta E$  is negligible. It is therefore reasonable to take  $\Delta E$  proportional to  $N$ , but other powers of  $N$  are also permissible. In any case the differences between  $S_B^{eq}$ ,  $S_F^{eq}$ , and  $S_G^{eq}$  are of order  $\log N$  and may therefore be neglected.

#### 4. NON-EQUILIBRIUM STATES

While the system moves according to its equations of motion, the variable  $a_0 = A^{(0)}(p, q)$  is constant, whereas the other coordinate in  $a$ -space, namely  $a_1 = A^{(1)}(p, q)$ , depends on time.  $a_1$  fluctuates up and down, but these fluctuations are only small compared to the main trend of  $a_1$  towards its equilibrium value zero. Hence it is possible to define a quantity  $\alpha_1(t)$  which follows the main trend of  $a_1$ , but in which the fluctuations have been smoothed out. This  $\alpha_1$  may be regarded as the macroscopically observed quantity corresponding to the microscopic  $a_1$ . Of course,  $\alpha_1$  can only be defined with an inaccuracy of the order of the fluctuations, but that is good enough for a thermodynamical quantity. The size of the fluctuations will be of the order of the equilibrium fluctuations, that is, of order  $g^{-\frac{1}{2}}$ .

Because of these fluctuations of  $a_1$ , the value of  $S_B(a)$  will also fluctuate

around an average trend given by

$$S_B(\alpha) = k \log G(a_0, \alpha_1) = S_B^{\text{eq}} - \frac{1}{2}kg\alpha_1^2 + \frac{1}{2}k \log (g/2\pi). \quad (5)$$

This expression is not exactly equal to  $S_B(a)$ , but it provides a smoothed curve whose deviation from the actual fluctuating curve is of order

$$\delta S_B = \left| k \frac{d \log G(a_0, \alpha_1)}{d\alpha_1} g^{-\frac{1}{2}} \right| = kg^{\frac{1}{2}} |\alpha_1|.$$

This has to be compared with  $|S_B - S_B^{\text{eq}}|$ :

$$\frac{\delta S_B}{|S_B - S_B^{\text{eq}}|} = \frac{1}{|g^{\frac{1}{2}}\alpha_1|}.$$

Now a state of the system can only be distinguished macroscopically from equilibrium, if  $\alpha_1$  is far outside the range of the equilibrium fluctuations, i.e., if

$$g\alpha_1^2 \gg 1.$$

Hence for all such states the error in (5) is much smaller than  $|S_B - S_B^{\text{eq}}|$ ; in fact for a macroscopic departure from equilibrium the relative error is of order  $N^{-1}$ .

For the calculation of  $S_F$  and  $S_G$  a probability distribution  $P(a, t)$  has to be introduced. In fact, the use of a probability distribution may be regarded as a more systematic device for carrying out the above smoothing process. Again let  $P(a_0, a_1, t)$  be zero outside the energy shell; inside the energy shell its time dependence is governed by the so-called master equation

$$\frac{\partial P(a_1, t)}{\partial t} = \int \{W(a_1, a_1') P(a_1', t) - W(a_1', a_1) P(a_1, t)\} da_1'.$$

It has been argued before <sup>6)</sup>, that this equation has solutions that are approximately given by

$$P(a_1, t) = \frac{1}{\Delta E} \sqrt{\frac{\gamma}{2\pi}} e^{-\frac{1}{2}\gamma(a_1 - \varphi(t))^2}. \quad (6)$$

Here  $\varphi(t)$  is a solution of the macroscopic phenomenological equation for the irreversible behavior of  $a_1$ ; for instance in the linear case it has the familiar form of an exponential decay:  $\varphi(t) = \varphi(0)e^{-\lambda t}$ . The parameter  $\gamma$  describes the instantaneous width of the distribution; in general it also depends on  $t$ , but it will always be of the same order of magnitude as  $g$ .

(6) constitutes a sharp Gaussian peak, which moves bodily along the  $a_1$ -axis. The position of the peak is given by  $\varphi(t)$ ; its width  $\gamma^{-\frac{1}{2}}$  is small compared to  $\varphi(t)$  as long as equilibrium has not yet been reached. This way of describing the non-equilibrium state is essentially different from the one used by Teitler and Wallis <sup>7)</sup>. They postulate an expression similar to (6), but subsequently expand it with respect to  $\varphi(t)$ . This

expansion is only correct if  $\varphi$  is well inside the equilibrium fluctuations, in which case however the state cannot be distinguished from equilibrium by a macroscopic observer.

The Gaussian form of the distribution (6) is convenient for computations, but our results are more general. What matters is only that the distribution is a peak whose width is small compared to its distance from equilibrium. In that case it is possible to introduce a macroscopic variable  $\alpha_1(t)$  to describe its position without its precise shape. In case of a Gaussian distribution the most obvious and convenient choice is  $\alpha_1(t) = \varphi(t)$ , but this is by no means necessary. Actually  $\alpha_1$  is defined only with an accuracy of order  $\gamma^{-\frac{1}{2}}$ .

Substituting (6) in  $S_F$  one obtains

$$S_F = S_F^{eq} - \frac{1}{2}kg\alpha_1^2 - \frac{1}{2}k(g/\gamma). \tag{7}$$

The last term is of order  $k$ , whereas the second term  $-\frac{1}{2}kg\alpha_1^2$  is larger by a factor of order  $N$  for any macroscopic departure from equilibrium. Similarly one obtains for the Gibbs entropy

$$S_G = S_G^{eq} - \frac{1}{2}kg\alpha_1^2 - \frac{1}{2}k \{ (g/\gamma) - 1 - \log(g/\gamma) \},$$

which also differs from  $S_T$  only by a term of order  $k$ .

These two expressions for the entropy may be looked at in the following way. They are functionals of the distribution  $P(a_1, t)$ , but owing to the special form (6) of  $P$  they decompose in three terms. *The first term* is the entropy of the equilibrium distribution. *The second term* is the entropy decrease caused by the fact that the peak is centered at  $\alpha_1$ , away from the equilibrium and therefore unfavorable as far as extension in phase space is concerned. Finally there is *a third term* depending on the width of the peak. This term is different for  $S_F$  and  $S_G$ . However, it is negligible compared to the second term, provided that the peak is situated well outside the range of the equilibrium fluctuations. This must indeed be true for all states that can be distinguished from the equilibrium state by a macroscopic observer.

### 5. THE INCREASE OF ENTROPY

From experience we know that the macroscopic, thermodynamical entropy increases monotonically with time and is equal to its maximum value (consistent with the given energy value) in equilibrium. The same behavior can be proved for  $S_G$  in a general way. Indeed, using the master equation and the symmetry relation for the transition probabilities (law of detailed balancing):

$$W(a, a') G(a') = W(a', a) G(a),$$

one finds

$$\frac{dS_G}{dt} = -k \int \frac{\partial P(a)}{\partial t} \log \frac{P(a)}{G(a)} da =$$

$$\begin{aligned}
&= -k \iint W(a, a') G(a') \left( \frac{P(a')}{G(a')} - \frac{P(a)}{G(a)} \right) \log \frac{P(a)}{G(a)} da da' \\
&= \frac{1}{2} k \iint W(a, a') G(a') \left[ \left( \frac{P(a)}{G(a)} - \frac{P(a')}{G(a')} \right) \left( \log \frac{P(a)}{G(a)} - \log \frac{P(a')}{G(a')} \right) \right] da da'.
\end{aligned}$$

Since both factors in this integrand are non-negative, the integral is non-negative. Moreover, it can only be zero if  $P(a)/G(a)$  has the same constant value for all  $a$ 's that are linked (directly or indirectly) by non-zero transition probabilities. The value of this constant is found from the normalization of  $P(a)$ , and determines  $S_G^{\text{eq}}$  as given in (4). — Of course, this simple proof is only possible because all real difficulties of statistical mechanics occur in the derivation of the master equation.

This result implies that, for a macroscopic observer,  $S_B$  and  $S_F$  must also increase monotonically. Of course, the monotonic increase of  $S_B$  and  $S_F$  also follows from their explicit values (5) and (7), because  $\alpha_1$  decreases with time\*). However, this argument is based on more detailed information than the one given above for  $S_G$ , nor does it tell anything about the small-scale variations. In fact, it is evident that on a small scale  $S_B(a(t))$  cannot vary monotonically, because it fluctuates even in equilibrium.

## 6. DISCUSSION

Since the three statistical interpretations of the thermodynamical entropy lead to numerically indistinguishable results, they are equally correct\*\*). The macroscopic entropy may be identified with any one of them. We shall here discuss the advantage and disadvantage of each.

If one insists that the microscopic state of a system should be described by a single point in phase space, only the Boltzmann expression for the entropy is available. But if one chooses to introduce an ensemble, either the Fierz or the Gibbs expressions may be used. In quantum mechanics, however,  $S_B$  can never be used, because a single pure (not stationary) state already corresponds to a probability distribution in  $a$ -space<sup>8</sup>).

A distinction between  $S_F$  and  $S_G$  is obtained by noting that several properties that are true on a *macroscopic* scale for the thermodynamical entropy, are also *exactly* true for  $S_G$ , but only approximately for  $S_F$ . Such properties are

- (i)  $S_G$  increases monotonically (see previous section).
- (ii)  $S_G$  takes its maximum value for the equilibrium distribution  $P(a) \propto G(a)$ .
- (iii)  $S_G$  is invariant for a change of coordinates in  $a$ -space.

\*) When there are more variables,  $\alpha_1, \alpha_2, \dots$ , they need not individually decrease monotonically but the quadratic expression that represents the entropy does.

\*\*\*) This point of view is contrary to that of Fierz, who feels that  $S_F$  is better "begründet" than  $S_G$ .

The fact that  $S_F$  is not invariant is particularly troublesome when discrete phase cells are used, because in that case the value of  $S_F$  depends on the rather arbitrary size of the cells. Of course, for any reasonable choice for the size the additional constant in  $S_F$  is again negligible, as was shown by Fierz.

An unpleasant feature of  $S_G$  is that it depends on the thickness  $\Delta E$  of the energy shell in such a way that  $\Delta E$  cannot be made to vanish. The reason is that  $S_G$  is defined for a probability distribution in the space of *all* variables  $a$ . If the value of  $a_0$  is determined exactly, this distribution becomes infinitely narrow and infinitely high, consequently the amount of information becomes infinite, so that  $S_G$  tends to  $-\infty$ . Hence it is impossible to go to the limit of an infinitely thin energy shell, when the expression  $S_G$  is used for the entropy. However, the following modification of the expression for the entropy will make it possible.

A microcanonical distribution on an infinitely thin shell with energy  $E$  is determined by

$$P(a_0, a_1) = p(a_1) \delta(a_0 - E).$$

Here  $p(a_1)$  is a probability distribution on the hypersurface  $a_0 = E$  in  $a$ -space (In the present case this hypersurface reduces to a line.) The normalization condition reads

$$1 = \iint P(a_0, a_1) da_0 da_1 = \int p(a_1) da_1.$$

Now define

$$\bar{G}(E; a_0, a_1) = G(a_0, a_1) \delta(a_0 - E).$$

Then it is possible to write a new expression for the entropy, viz.,

$$\begin{aligned} \bar{S} &= -k \iint P(a_0, a_1) \log \frac{P(a_0, a_1)}{\bar{G}(E; a_0, a_1)} da_0 da_1 \\ &= -k \int p(a_1) \log \frac{p(a_1)}{G(E, a_1)} da_1. \end{aligned}$$

(The cancelling of  $\delta$ -factors in numerator and denominator is readily justified by performing the limiting process.) This is also the expression to which information theory leads for a surface distribution. It has the same properties (i), (ii), (iii) that  $S_G$  has. In fact, its connection with  $S_G$  is simply

$$\bar{S} = \lim_{\Delta E \rightarrow 0} (S_G - k \log \Delta E).$$

Hence the value of  $S$  need not be computed separately. In particular one has on account of (4),

$$\bar{S}^{eq} = k \log G(E, 0) - \frac{1}{2}k \log (g/2\pi),$$

which happens to coincide exactly with  $S_B^{eq}$  as given by (2).



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