Entropy, or Entropies, in Physics?

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Abstract.

Entropy and its physical meaning have been a problem in physics almost since the concept was introduced. The problem is exacerbated by its use in both statistical thermodynamics and information theory. Here its place in classical thermodynamics, where it was introduced originally, and in these other two areas will be examined and hopefully some light will be cast on the present position.

Introduction.

The idea of entropy, or at least its change, first arose in classical thermodynamics via deductions made from the basic traditional forms of the Second Law. Either the Kelvin or Clausius form of that law was used to show mathematically that that the quantity representing a change in heat, $d'Q$, an inexact differential, possessed an integrating factor which was the absolute temperature $1/T$. The product $d'Q/T$ was then a total differential denoted by dS, and referred to as a change in entropy. At a later stage, when it became desirable to consider the properties of systems, particularly gases, with large numbers of particles, statistics were introduced and this led to the birth of statistical thermodynamics. Soon quantities in statistical thermodynamics were identified, not unreasonably, with quantities in classical thermodynamics but this identification seems to have been assumed valid, rather than actually proved valid. While all this was occurring, information theory was being developed separately but, in a classic book by Brillouin[1], an apparent link between statistical thermodynamics and information theory was established although this suggested link was hinted at by Shannon in his classic article of 1948[2]. In all three areas, a function termed *entropy* appears but the question of whether or not these three are identical, or not, always seems to be being assumed, not proved. The background to each of these three *entropies* will be looked at in separate sections, before considering their possible inter-relationship.

Classical Thermodynamics.

In the usual approaches to classical thermodynamics, the First Law; Energy is conserved when heat is taken into account,is often represented by the mathematical equation

$$d'Q = dU - d'W$$

where the three terms represent changes in heat, internal energy and work respectively. $d'Q$ and $d'W$ are not differentials of functions of state and the dashes indicate this and the fact that, mathematically, the first and third terms are inexact differentials.

The Second Law is then introduced into the discussion in one of its fundamental forms due to Kelvin or Clausius. In their modern wording, these are:-

Kelvin:

It is impossible to transform an amount of heat completely into work in a cyclic process in the absence of other effects.

and

Clausius:

It is impossible for heat to be transferred by a cyclic process from a body to one warmer than itself without producing other changes at the same time.

As may be seen[3], either of these forms, but usually that due to Kelvin, may then be used to show via a mathematical argument that the inexact differential $d'Q$ possesses an integrating factor which turns out to be the reciprocal of the absolute temperature, T. It is then customary to write

$$d'Q/T = dS$$

where dS simply represents the resulting exact differential. In the derivation, no direct physical interpretation is assigned to dS but, customarily, it is deemed to be the change in a quantity termed the entropy. However, here, *entropy* is simply the name given to the quantity represented by the symbol S but it should be noted that, in classical thermodynamics, the change in this quantity is irrevocably linked to a change in heat experienced by the system under consideration.

The equation representing the combined form of the First and Second Laws is then:

$$TdS = dU - d'W.$$

Again, if the work done in compressing a fluid is being considered, this equation takes on the familiar form:

$$TdS = dU + pdV,$$

where p and V represent the pressure and volume as usual. Note though that this is not the general form of the equation representing the combined First and Second Laws; it refers to a quite specific set of circumstances.

If attention is restricted to systems for which the entropy is an extensive variable then the discussion is easily extended[2] to open systems and again considering the special case of compression of a fluid, this latter equation becomes

$$TdS = dU + pdV - \mu dN, \qquad \text{(i)}$$

where μ and N represent the chemical potential and number of particles respectively.

All of the preceding discussion is restricted to so-called quasi-static processes. If considerations are extended to include non-static processes, it may be shown that, for non-static adiabatic processes, the inequality

$$dS \geq 0.$$

If the entropy, S, is a state function, this inequality is a statement of the principle of increase of entropy. However, it is vitally important to realise that this result is *derived* from the basic form of the Second Law; it is ***not*** an actual statement of the Second Law. Obviously, there are occasions when the entropy of a system does decrease; for example, in a cyclic situation, such as a Carnot cycle, if the entropy increases in one section, there must a corresponding decrease in another to ensure a successful completion of the cycle. Also, from its actual derivation, it is immediately obvious that, if heat is added to a system, the entropy change is positive while, if heat is taken from a system, the entropy change is negative. Hence, at least as it stands with no stated limitations, claims that the principle of entropy increase is a statement of the Second Law[1,4] are not accurate and could be thought misleading. This is particularly true when it is remembered that there is controversy[5] over whether the entropy is always a state function in classical thermodynamics.

Statistical Thermodynamics.

In statistical thermodynamics, there are various approaches to introducing the topic but all seem to rely on equation (i) above to secure a link with the quantities of importance in classical thermodynamics. Hill[6] devotes an entire section to the association of thermodynamic variables with quantities of statistical mechanics. His approach is to consider the various ensembles separately, to associate immediately the internal energy of classical thermodynamics with the ensemble average of the internal energy. He then proceeds to evaluate the expression for the total derivative of this ensemble average in terms of the independent variables appropriate for the ensemble under consideration and then to compare the resulting equation with equation (i) above. In this way, he is able to identify the entropy, S, as

$$S = -k \sum p ln p \qquad \text{(ii)}$$

where p represents the expression for the probability in the relevant ensemble. For example, this leads as far as the grand canonical ensemble is concerned to the identification

$$\frac{pV}{kT} = ln \Xi ,$$

where Ξ represents the grand partition function and, as usual, p represents the pressure, V the volume, k Boltzmann's constant, and T the absolute temperature. By noting further that, if F is the free energy

$$dF = -SdT - pdV + \mu dN,$$

where, additionally, μ represents the chemical potential and N the number of particles, then, once the expression for the pressure is known, those for the entropy, S, and number of particles, N, eventually follow from

$$S = V\left(\frac{\partial p}{\partial T}\right)_{V,\mu} \quad \text{and} \quad N = V\left(\frac{\partial p}{\partial \mu}\right)_{V,T}.$$

The relevant expression for the internal energy, U, then follows from

$$U = TS - pV + \mu N.$$

Hence, the expressions for all the important functions of classical thermodynamics follow by making use of well-known expressions from classical thermodynamics in what might appear to be a circular argument.

In this approach as in others in statistical mechanics/thermodynamics, there is no direct mention of any heat exchange at any point but it seems that, because equation (i) is assumed, success of sorts in linking classical thermodynamics with statistical mechanics/ thermodynamics is assured. In reality though, it seems the entropy of classical thermodynamics is assumed the same as that of statistical mechanics/thermodynamics. However, the nature of the above quoted expression (ii) for the entropy in statistical mechanics/thermodynamics bears no obvious resemblance to that of classical thermodynamics. In classical thermodynamics, as stated already, the entropy is linked irrevocably with the change of heat; here the expression above indicates that the entropy of statistical mechanics/thermodynamics is, first and foremost, linked to a probability distribution. This is why the question of whether or not the two entropies are the same must arise.

It should be noted that, although there are only two fundamental categories of thermodynamic theories which are covered by the classical approach outlined in the first section of this article and the statistical or probabilistic approach being discussed briefly here, there are several approaches to this second approach. Another is beautifully outlined in the book by Lavenda[7]. Basically he derives all the accepted results via use of Gauss' principle and extensive use of error laws; error laws which are discussed in minute detail in Keynes' book on probability[8]. This rather elegant approach has much to commend it but, yet again, the link between probabilistic average values is made by assuming such – especially the entropy – are identical with the corresponding values in classical thermodynamics. Hence, the query raised in relation to the approach of Hill arises again and does so in all approaches to establishing a theory of statistical mechanics /thermodynamics.

However, it must always be born in mind that statistical mechanics/thermodynamics has proved to be an eminently successful branch of physics over many years. Nevertheless, the question of the actual equivalence of the entropy functions of classical and statistical thermodynamics remains a very real one and is one which should not be dismissed lightly. It is probably true to say, though, that this question has only arisen largely because of the rise in usefulness of information theory in both physics and, indeed, other branches of science such as biology and medicine.

Information Theory.

Possibly the best way to approach the introduction of the notion of entropy in information theory is to consider the way Shannon himself introduces the topic. To do this, consider Shannon's own wording beginning on page 48 of the mentioned book:- he begins by pointing out that, up to that point in his presentation, a discrete information source has been represented by a Markov process. He then poses the question of whether or not it is possible to '*define a quantity which will measure, in some sense, how much information is "produced" by such a process, or better, at what rate information is produced*'.

He continues by considering a set of possible events whose probabilities of occurrence are p_1, p_2,…., p_n. These probabilities are all that is known concerning which event will occur. The question than is whether or not a measure of how much "choice" is involved in the selection of the event or of how uncertain the outcome is may be found. If such a measure, say $H(p_1,p_2,\ldots,p_n)$, exists it is claimed that it is reasonable to require the following properties for it:

- (i) *H* should be continuous in the p_i
- (ii) If all the p_i are equal, $p_i = 1/n$, them *H* should be a monotonically increasing function of *n*.
- (iii) If a choice be broken down into two successive choices, the original *H* should be the weighted sum of the individual values of *H*.

On the basis of these required properties, it is shown in appendix 2 (pages 116-8) of the quoted book that the only *H* satisfying these three assumptions is of the form:

$$S = -K\sum_{i=1}^{n} p_i log p_i \qquad \text{(iii)}$$

where *K* is a positive constant which merely amounts to a choice of a unit of measure. Shannon points out that expressions of this form '*play a central role in information theory as measures of information, choice and uncertainty*'. He also goes on to point out at this very stage in his discussion that 'the form of *H* will be recognised as that of entropy as defined in certain formulations of statistical mechanics where p_i is the probability of a system being in cell *i* of its phase space. Of course, in statistical mechanics/ thermodynamics, the constant *K* is the Boltzmann constant represented by *k*. Again at this point in his discussion, Shannon proceeds to say that '*we shall call*' expression (iii) above the entropy of the set of probabilities $p_1,\ldots,p_n$. He also says that , if *x* is a chance variable, we will write $H(x)$ for its entropy; thus x is not an argument of a function but a label for a number, to differentiate it from $H(y)$ say, the entropy of the chance variable y.

It is quite clear from this abbreviated introduction to a basic formula of information theory that its introduction is purely mathematical and does not rely at all on any genuine physical input – certainly nothing remotely connected with notions of classical thermodynamics. Interestingly, the outline of this derivation also serves to emphasise that the same is basically true of the introduction of the entropy concept into statistical mechanics/thermodynamics. Also it seems the introduction of a link between the entropy functions of information theory and classical thermodynamics followed the route outlined in Brillouin's book[1]; that is that it was simply noted that the entropy expressions of information theory and statistical mechanics/thermodynamics had the same mathematical form and so were assumed to be same. The link with classical thermodynamics then followed via the statistical mechanics link with that subject. Hence, when examining the origins of the three entropy functions, it quickly becomes apparent that as progression occurs from that for classical thermodynamics to statistical mechanics/thermodynamics to information theory, actual physical ideas play a gradually decreasing role and heat only appears in the first of these derivations. These are all points which must come into consideration when examining the claim, implicit at least in some writings, that the entropy functions of classical thermodynamics, statistical mechanics/ thermodynamics and information theory are identical functions.

Further Comments.

In the above, very brief introductions to the origins of the entropy concept, or possibly concepts, in classical thermodynamics, statistical mechanics/thermodynamics and information theory have been presented. It is clear immediately that, in the first case, the function termed the entropy is irrevocably linked to heat while this is certainly not so in the other two cases discussed. One can, however, see the possibility of a real link between the concepts of entropy in statistical mechanics/thermodynamics and information theory. Indeed, Lavenda has commented more than once that, in retrospect, it appears unfortunate that the two subjects developed independently of one another. Possibly more and quicker progress could have been achieved if this had not been so. Also, much duplication of effort could have been avoided. However, that is not the case. The position as of now is then that the entropy concepts of statistical mechanics/thermodynamics and information theory do have much in common but their link with the entropy of classical thermodynamics may only be described as tenuous. As pointed out already, the entropy of classical thermodynamics is linked with the concept of heat and nothing can change that. The other two entropies are introduced with no mention of heat or heat exchange and neither can be linked directly with the concept of heat. Further, all the links with classical thermodynamics introduced into statistical mechanics appear to be done ad hoc; rarely, if ever, is any rational physical justification for the introduction of the functions and equations of classical thermodynamics advanced and yet it is just this introduction which enables so much to be accomplished physically in that branch of physics. Undoubtedly, the route taken has produced many satisfactory results but it must be wondered if that is more by luck than judgement?

Looking especially at the approach of such as Hill and remembering the successes of statistical mechanics/thermodynamics, it is difficult to believe the theory incorrect. However, when the subject of the relevant entropies arises, it is equally difficult to accept that they are one and the same function as their two bases are so completely different. When information theory enters the picture, the connection between the entropies – if, indeed, one exists – becomes even more vague and difficult to accept. In fact, it might be wondered if this is, at partially, behind the somewhat peculiar conjecture of Landauer. In an article of 1961, Landauer suggested that erasure of information is a dissipative process and, therefore, that a small quantity of heat is necessarily produced when a classical bit of information is deleted. This seems another way of artificially introducing the notion of heat into an area of physics where it simply doesn't appear naturally. A quick glance at some of the basic notions of information theory as explained by Shannon[2] and, possibly more obviously, by Brillouin[1] would seem to suggest that this could have been the case and Landauer was, in a sense, inverting the link between entropy and heat which occurs quite naturally in classical thermodynamics. It might be noted that more appeared querying Landauer’s conjecture in an earlier article[9].

However, these days, more and more applications for all of these traditionally physics’ topics are appearing in the biological sciences and medicine. Here different problems are seemingly encountered which appear far removed from the notions of heat engines which led originally to the subject now known as classical thermodynamics. Nevertheless, if classical thermodynamics is to apply, its basic laws must apply and that means that, even if the wording is altered to fit the new regime, the fundamental tenets of the second law must apply too; that is, reference must be made to something not being possible in a cycle in the absence of other effects.

Although not related directly to entropy, it is interesting to note at this point that Ho[10] makes mention of this and refers back to a much earlier article by MacClare[11]. However, Ho refers to an abbreviated form of the second law, as advanced by MacClare, which states that

Useful work is only done by a molecular
system when one form of stored energy is
converted into another.

where by stored energy is meant any form of energy that does not equilibrate, or degrade, into heat in the interval τ, with τ being a standard time greater than that necessary for thermal energies to equilibrate throughout the system and reach equilibrium. However, the drawback with this statement and a modified one due to Ho is that there is no mention of cycles or other conditions. It should be noted though, that, in his original article, MacClare did advance the following form of a modified second law[11]:

It is impossible to devise an engine, of any
size whatever, which, acting in a cycle which takes a time τ, shall produce no
effect other than the extraction of energies, which have equilibrated with each
other in a time less than τ, from a reservoir at one temperature and the
conversion of these energies into a form in which they would remain stored for
longer than τ; either at a higher temperature, or in a population inversion.

He continued to point out that this statement clarifies what the second law actually forbids in practice and shows that weights lifted by Brownian motion have not had any useful work done on them. Unfortunately in some ways, he then proceeds to express the second law in the previously mentioned form which MacClare himself describes as a very economical form. However, he points out that the abbreviated statement does serve to define useful work and that, together with the definition of stored energy he gives, makes it clear that the statement applies at the molecular level as well – something crucial for biological applications. He concludes by noting that this "means that it follows from the second law (when that law is properly understood) that if energy is stored initially in a single molecule then, once that energy is allowed to exchange with thermal energies, useful work can no longer be done with it." Nevertheless, it is a pity that it is this abbreviated form which is now quoted because it omits those two points crucial to the second law – the fact that something is not possible in a cycle in the absence of other effects.

It should be noted at this juncture that MacClare was concerned with examining the molecular nature of living things and was interested, in particular, in whether or not such systems could work in the same way as ordinary chemical machines. To this end, he made some extremely useful points concerning the supposed statistical nature of the second law and also made some insightful comments regarding the nature of the quantity referred to as work. On this second point, he was at pains to distinguish between doing work usefully and wastefully and it is for that reason he introduced the terms *stored energy* and *useful work* referred to above.

The paper by MacClare and the article by Ho are important in that they draw attention to the fact that modifications to some wording in classical thermodynamics must be made in order to make that subject directly applicable in the biological sciences. This is something which needs addressing and clarifying as a matter of urgency.

Concluding Comments.

It is virtually impossible to end this article with a definite conclusion. Suffice it to say, though, that serious doubts must exist concerning the equivalence of the entropy function of classical thermodynamics and the corresponding functions of statistical mechanics and information theory; the bases of the functions are totally different and the link between those of classical thermodynamics and statistical mechanics seems contrived in order to produce the statistical thermodynamics theory known and used, albeit with apparent great success, today.

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