Chapter 11
Physics Education Research and the Foundations of Physics: A Case Study from Thermodynamics and Statistical Mechanics

David Sands

Abstract The connection between mathematics and physics poses problems for students, but even professional physicists do not always notice when mathematical treatments fail to reflect physical processes. By way of example, I draw on the foundations of thermodynamics, which is a highly mathematical but conceptually challenging subject. The failure of mathematics to connect to physics concepts, in particular energy conservation, raises a number of questions. First, how is it that generations of professional physicists have been seduced by the elegance of mathematics into overlooking underlying difficulties with the physics? Secondly, what can this tell us about the *how* of physics: how is it done, how do we justify a theory? Thirdly, should PER encourage us to look more critically at the fundamental foundations of physics, and if so, what does it reveal about the way we should be teaching these subjects? Not all of these questions can be answered yet, but in this chapter I illustrate some of the more profound mathematical difficulties in thermodynamics and briefly discuss what approach to teaching thermodynamics might fruitfully be taken.

11.1 Introduction

At the GIREP-ICPE-EPEC conference in Dublin, 2017, I presented an argument that the foundations of thermodynamics were flawed and asked how this should affect the approach to the teaching of thermodynamics. This chapter is on the same topic and inevitably draws on many of the same arguments, so some overlap is unavoidable. However, the arguments against the concept of thermodynamic entropy as a property of a body are numerous and in this work I shall attempt to present the case against entropy slightly differently.

D. Sands (✉)
Department of Physics and Mathematics, University of Hull, Hull, UK
e-mail: D.Sands@hull.ac.uk

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Just what is it about entropy that I disagree with? Simply that entropy is not a property of a body and that Clausius erred in his derivation of the fundamental inequality of irreversible thermodynamics, namely;

$$TdS \geq dQ \tag{11.1}$$

I shall argue in this chapter that this expression is not consistent with energy conservation as expressed in the First Law and that its use as the basis of the commonly accepted form of the Second Law due to Clausius, which holds that the entropy of the universe can never decrease, is incorrect. To begin, I go back to foundations of thermodynamics to review the origin of the concept of entropy, starting with Carnot and Clausius. Carnot idealised the operation of a heat engine and paved the way for people like Clausius and Thompson (Kelvin) to incorporate the equivalence of heat and work into a theory of thermodynamics that has passed down the generations almost unchanged at its core.

Clausius reworked Carnot's theory in 1850 (Clausius 1898) to take into account the change in the theory of heat from a material substance, caloric, to idea that heat is motion and developed the modern notion of reversibility from the idea of a reversible cycle. It is perhaps not widely appreciated, however, that Clausius and Kelvin differed fundamentally in their view of thermodynamics (Magie 1899). Indeed, the very word, "thermodynamics" was coined by Kelvin to describe the idea of using heat to produce work and vice versa, generating heat from work. Kelvin was concerned with cyclic processes, without which a heat engine cannot operate. It was implicit in everything he wrote and is central to his statement of the Second Law: it is impossible to convert an amount of heat completely into work in a cyclic process in the absence of other effects. Kelvin's statement is simple and intuitive. Work can be done during the expansion stage of a cycle but the piston has to be returned to the starting position with the working fluid back at the starting state for the engine to continue working. This also requires work, which is derived from a portion of the heat taken in from the hot reservoir. Clausius' view of thermodynamics was much less intuitive.

Clausius phrased his statement of the Second Law as the impossibility of transferring heat from a cold to a hot body without some other effect also occurring at the same time. Although not explicitly stated, this also relies on the existence of a cyclic process and indeed the proof of the equivalence of Kelvin's and Clausius' different forms of the law usually considers two cyclic processes in tandem, with one operating as a refrigerator converting work into heat and the other as a heat engine converting heat into work. Violation of one form of the law leads to violation of the other (Zemansky 1968). The cyclic process is therefore central to the foundations of thermodynamics and it was Carnot's innovation to represent the ideal, reversible heat engine as an ideal cycle comprising alternate isothermal and adiabatic processes. Ironically, it was Kelvin who followed Carnot most closely in regarding the cycle itself as reversible, but it was Clausius' ideas that gained prominence and for him the separate stages of the cycle were themselves reversible processes.

The modern notion of a reversible process as quasi-static is derived directly from Clausius, but curiously, the notion of a quasi-static process as reversible has never, to my knowledge, been questioned. Quite possibly, this is because the Carnot cycle comprises four stages which can be represented as occurring along contours in thermodynamic phase space defined by either constant temperature or zero heat flow and the differential form of work, $P\mathrm{d}V$, is integrable between any two points along such contours. Thus, mathematically at least, the work done by the gas between two states, denoted by, say, A and B, on any such contour is,

$$W = \int_A^B P\mathrm{d}V = -\int_B^A P\mathrm{d}V \tag{11.2}$$

The key question is whether there is any physical process that corresponds to this mathematical abstraction. If not, the separate stages of Carnot's cycle are not in themselves reversible and we should consider, in line with Carnot and later Kelvin, the reversibility of the cycle. Moreover, entropy cannot be considered a property of a body.

This last argument is quite subtle and not so easily comprehended, but it can be understood with reference to cyclic processes. It was Clausius himself (1898) who argued that within a cyclic process,

$$\oint \frac{\mathrm{d}Q}{T} \leq 0 \tag{11.3}$$

The equality applies to a reversible cycle, such as Carnot's, and the inequality applies to a cycle that contains an irreversible process. Although Clausius claimed that this was susceptible to mathematical proof, there is scant evidence in the literature that he actually did prove it, though it appears to hold in practice in as much as there are no reported violations within the literature. The irreversible process that Clausius considered and which demonstrates this theorem in practice was the Joule expansion, in which a gas expands freely into a vacuum. There is no work done, no heat flow, and therefore no change in internal energy during such a process. In order to restore the initial state following such an expansion it is necessary to compress the gas, which requires work. If there were no flow of heat out of the gas its temperature would rise and the initial state could not be restored. No matter whether it occurs during the compression or after, the internal energy of the gas must be reduced and this inevitably requires a flow of heat out of the gas. If a flow of heat out of a body is defined as negative, then the inequality in Eq. (11.3) holds. If entropy is a property of a body, then it is clear that it has decreased as a consequence of this net outflow of heat. If further, the entropy is considered to have a unique value in a given thermodynamic state, then it must have increased during the irreversible process and Eq. (11.1) in seen to hold. Moreover, as the body itself has returned to its initial state with no change in entropy, the inflow of heat into the environment represents a positive increase in entropy and Clausius' view of the

Second Law that the entropy of the universe can only increase or remain the same, is seen to operate.

At the heart of this view is the relationship between Eqs. (11.1) and (11.3) and the notion that entropy is property of a body with a unique value in a thermodynamic state. A body is defined here as simply any collection of atoms or molecules in whatever state, solid liquid or gas. This phrasing makes the distinction between entropy as a state function, which is essentially a mathematical notion, and entropy as a property of a body, which is a physical idea. The connection between the two is an area that has been neglected in the literature on entropy, but lies at the heart of the present discussion. In relation to physics education research, the link between mathematics and physics should be central to any physics education programme, but I will argue here that the history of entropy shows that even professional physicists can put mathematics first ahead of physics. In this chapter, the connection between the law of increasing entropy, as expressed by Eq. (11.1) and the law of conservation of energy will be examined with reference to particular examples. In addition, the relationship between the mathematical idea of a state function and the corresponding physical properties will also be examined and examples of students' confusion over entropy will be presented.

11.2 Entropy and Energy Conservation

The preceding example on the free expansion illustrates the fundamental problem of the notion of the entropy of a body. As there is no change in internal energy during the free expansion, there is also no change in temperature. Even if it is argued that during the expansion the state of the gas is not well defined, the quantity TS, which has the units of energy, must be defined for the initial and final states. The change in the Gibbs free energy is given by the difference, yet there is no change in U, no heat flow and no work done. We can meaningfully ask about the physical meaning of the Gibbs free energy in the light of this change.

This difficulty was built into the structure of thermodynamics by Clausius, as summarised in the 1898 (Clausius 1898) collection of his nine Memoirs. It is evident in all his early writings that Clausius was interested in what he referred to as, "internal work", which is the work associated with inter-particle forces when a gas is either compressed or expands. In treating internal work, Clausius borrowed from his earlier work on cyclic processes: "*… as there is no essential difference between interior and exterior work, we may assume with certainty that a theorem which is so generally applicable to exterior work cannot be restricted to this alone*". In fact, there were two theorems in Clausius' view of thermodynamics, which Clausius explained as the equivalence of heat and work, or Joule's principle, and the equivalence of transformations. The latter will be unfamiliar to the modern physicist, as it is an obscure concept not taken up by Clausius' contemporaries and which has subsequently disappeared altogether from the thermodynamics lexicon. Clausius regarded two transformations as being equivalent in some way: the conversion of heat into work, and *vice versa*, in a cyclic process and the conversion of "heat at one temperature to heat at another temperature". Mathematically, the theorem of the equivalence of transformations is expressed by Eq. (11.3), though originally heat was defined such that the integral is positive for an irreversible cycle. It was sometime later that Clausius adopted the modern convention that negative heat corresponds to a heat flowing out of a body.

In referring to exterior work, Clausius meant the work produced by a heat engine. In an ideal reversible engine of the kind considered by Carnot, all the transformations are, to use Clausius' terminology, compensated by equivalent transformations and the equality in Eq. (11.3) applies. For example, the heat taken in from the hot reservoir is converted to work, but in returning the piston to its starting state work is converted to heat which is ejected to the cold reservoir. Both processes have the same equivalence value, Q/T. In an irreversible cycle, at least one of the transformations is uncompensated, leading to the inequality as previously discussed. In comparing internal work to external work, Clausius believed that there must be a similarly uncompensated transformation and actively sought an equivalent inequality. In consequence, he derived Eq. (11.1).

The essential difficulty with Clausius' work is that he did not base it on conservation of energy. The concept was not fully developed at the time and this can be seen in his approach to irreversible, noncyclic processes. Equation (11.3) for cyclic processes is fully compatible with energy conservation whereas Eq. (11.1) for noncyclic processes is not. In a cyclic process, an irreversible stage can by offset by some other process within the cycle in which heat is extracted to restore the original state, but this cannot occur in a single, noncyclic process. Clausius overcame this incompatibility in his Sixth Memoir by disregarding the work that is actually done in a process, which of course is governed by energy conservation, and looking instead at the work that might be done: "The law does not speak of the work which the heat *does*, but of the work which it *can do* . . ."; ". . .similarly, in the first form of the law, it is not of the resistances which the heat overcomes, but those of which it *can overcome* that mention is made". The emphasis is Clausius' and by this reasoning he introduced an inequality into the First Law of thermodynamics. In the following pages the consequence of this inequality are explored for a classical ideal gas subject to a change in the number of particles.

11.3 Extensivity, Entropy and Open Systems

Consider two systems at the same temperature and pressure. One contains N particles of a classical ideal gas in a volume V and the other $N + \delta N$ in a volume $V + \delta V$. Clearly, the difference in internal energy between the two systems is directly proportional to δN, so we have U, V and N all increasing by the same factor. Write,

$$\frac{\delta N}{N} = \frac{\delta V}{V} = \frac{\delta U}{U} = \alpha \tag{11.4}$$

Then,

$$N + \delta N = (1 + \alpha)N \tag{11.5}$$

If entropy is a homogeneous function of degree 1, then

$$S([1 + \alpha]U, [1 + \alpha]V, [1 + \alpha]N) = (1 + \alpha)S(U, V, N) \tag{11.6}$$

In other words, the entropy increases in proportion to the increase in the size of the system. This is standard and on the face of it presents no difficulties.

However, now consider what happens if we compress the second system isothermally through a volume change δV such that the work done is $P\delta V$. Energy conservation requires an outflow of heat corresponding to the work done, $P\delta V$, and the entropy of the systems decreases. However, we now have $N + \delta N$ particles in a volume V at temperature T and we would expect the entropy of this system to be greater than the entropy of N particles at V and T. If the entropy of the second system is now $(1 + \beta)S(U,V,N)$, where $\beta < \alpha$, then

$$(1 + \alpha)S(U, V, N) > (1 + \beta)S(U, V, N) > S(U, V, N) \tag{11.7}$$

Equation (11.7) appears to be consistent with known thermodynamics, but in fact there is a difficulty.

According to Landsberg [p128], the two systems considered above are closed, simple systems for which the equation,

$$T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V \tag{11.8}$$

holds. As closed systems, Eq. (11.8) cannot be used to describe the transformation from one to another at the same volume, otherwise we would have the simple result,

$$T\delta S = \delta U = \frac{3}{2}kT \cdot \delta N \tag{11.9}$$

This would lead to the difference in entropy being directly proportional to the number of additional particles, which is demonstrably not the case. In order to see this more clearly, consider the case when $\alpha = 1$. This corresponds to the famous Gibbs paradox in which there are two identical systems each containing N particles at temperature T and volume V separated by a partition. Removal of the partition creates a single, larger system with $2N$ particles at temperature T, and hence energy $2U$, in a volume $2V$. The entropy of this larger system is simply double that of each single system. If we were now to compress this larger system isothermally into half the volume, so that we had $2N$ particles in a volume V at temperature T, the entropy would have decreased and self-evidently the entropy would be less than twice the entropy of N particles in a volume V at temperature T. In short, the change in entropy cannot be given by the change in the number of particles and Eq. (11.9) is shown to be invalid.

Landsberg (1961) attempts to put the change in entropy of an open system on a firm mathematical footing and concludes on page 153 of his 1961 book that for a gas which is, “homogeneous in all its states of interest, and which contains only one type of molecule”, Eq. (11.8) can be extended to an equation of the form

$$T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V + T\left(\frac{\partial S}{\partial N}\right)_{U,V}\mathrm{d}N \tag{11.10}$$

Then, one has, by the “laws of partial differentiation” [p153],

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} \tag{11.11}$$

Applying Eqs. (11.10) and (11.11) to our two systems, we arrive at the conclusion,

$$T\delta S = \delta U - \mu\delta N = \left(\frac{3}{2}kT - \mu\right)\cdot\delta N \tag{11.12}$$

This is the desired result. We have shown that the entropy of $N + \delta N$ particles in a volume V at temperature T is greater than the entropy of N particles in a volume V at temperature T, but less than would be obtained if the entropy were simply proportional to the number of particles. This, then, accords with the thermodynamics of the simple systems we have so far developed.

11.4 Discussion and Conclusion

Having derived Eq. (11.12), it remains to show how this conflicts with energy conservation. If we have two systems at the same volume and temperature with the only difference between them being that one has δN more particles than the other, the difference in energy between the two systems is given by,

$$\delta U = \frac{3}{2}kT\cdot\delta N \tag{11.13}$$

Yet, Eq. (11.12) shows that there is some property of the body with the units of energy ($T\delta S$) that differs by an amount less than this. In other words, there is some energy contained in the quantity $-\mu\mathrm{d}N$ that offsets the increase in internal energy due to the increase in the number of particles. Thermodynamics gives us no clue as to the physical meaning of μ and the physics of the ideal classical gas in the form of kinetic theory gives no insight. Whilst the internal energy can be equated with the average energy of particles with a range of velocities given by the Maxwellian distribution, there is no quantity analogous to the chemical potential.

The physical meaning of μ and the validity of Eq. (11.11) can also be queried. It is not clear to this author that Eq. (11.11) is correct for a classical ideal gas. This equation is valid only if U and N are independent; that is, particle number N can be changed whilst holding both U and V constant. In a classical ideal gas N can be changed independently of V but not of U except at absolute zero, as shown by Eq. (11.13), so the partial differential in Eq. (11.10) cannot be applied.

It should be acknowledged that entropy might not be extensive, which would redefine the entropies of the different bodies we have discussed and alter the relationship between them. However, it is not clear that it would solve the problem, which fundamentally arises from the notion that a body in a particular state has a particular entropy. This can be illustrated by the following argument. It is reasonable to assume that entropy must in some way increase with the number of particles and that the entropy of $N + \delta N$ particles in a volume V at temperature T is greater than the entropy of N particles in a volume V at temperature T. We would expect some functional relationship between S and N which would permit partial differentiation, but in a classical ideal gas N can be varied independently of only T and V or, equivalently, P if V is allowed to vary with N. Expressing entropy as a function of T would make it difficult in general to combine the First and Second laws, but notwithstanding this difficulty let us suppose that we end up with something of the form,

$$\delta S(N) = \frac{\mu}{T}\delta N \tag{11.14}$$

Here, for complete generality μ can be positive or negative, though normally it is the latter. We are left with the difficulty that $T\delta S$ has the units of energy and the only change in energy of a classical ideal gas on changing the number of particles is given by Eq. (11.13). If the total change in entropy contains a term δU, the only value of μ that will satisfy energy conservation is zero, but if S does not explicitly depend on U but on T, μ must be equivalent to the average energy per particle in order to satisfy energy conservation. This is not the end of the difficulty, however, because the system can then undergo a Joule expansion to $V + \delta V$ in which there is no change in internal energy, but the quantity $T\delta S$ increases.

Whichever way we look at it, the concept of the entropy of a body would appear to be incompatible with energy conservation. The Joule expansion highlights the difficulty most clearly and illustrates the connection with Clausius' flawed reasoning. In a Joule expansion, $T\delta S$ is reckoned to increase by $P\delta V$ by comparison with the so-called equivalent process of a reversible isothermal expansion. The process is only equivalent in as much as the initial and final states are the same. However, in the isothermal expansion real work is done, but in the Joule expansion, no work is done and this is reflected in the fact that $P = 0$. This is not commonly appreciated, but follows from Newton's second law: if the molecules are expanding freely into a vacuum and do not change momentum through collisions with the wall of a container they are not themselves subject to a force and cannot exert a force. We therefore have an immediate conflict with the First Law that is built into the structure of thermodynamics via Clausius' assertion that, "The law does not speak of the work which the heat *does*, but of the work which it *can do* …". The idea that heat can do work is a direct consequence of the view of the time that heat was somehow converted into work, but we now know that work is a consequence of repeated collisions of particles on a piston. Heat flows into a gas to replace the energy lost during work and in this sense there is no such thing as isothermal heat flow. However, borrowing from the terminology of heat engines prevalent at the time of Clausius, we can regard heat as capable of doing work $P\delta V$. If, following Clausius, we use this work term to give the increase in entropy during an irreversible expansion, we are adding a term in energy that does not in fact reflect the physical processes and violates energy conservation.

This failure of the mathematics to reflect the physics has been overlooked by the majority of physicists for well over 160 years and consideration of this alone shows that the process of interpreting mathematical formalisms in terms of physics is not straightforward. It is perhaps not surprising that students struggle. It is over 10 years since Rebello, working with Dean Zollmann and others (Rebello et al. 2005), looked at the transfer of mathematical knowledge from one domain to another, but little progress seems to have made since then. Authors such as Karam (2014) and Redish and Gupta (2010) stress that understanding mathematics in physics is not just about understanding mathematical operations, but how those operations connect to and describe physics concepts. I suggest that we have only just begun to understand some of the complex interactions in not just learning physics, but in *doing* it and that this process of examining critically the way physics is done should impact on our understanding of the fundamentals.

Revisiting fundamental concepts and their connection to mathematical formalisms means keeping an open mind and rejecting a utilitarian approach. That is, just because a mathematical approach appears to be useful does not mean it is correct and it has been argued in this chapter that Clausius' conception of entropy was flawed in so far as it was based around the concept of transformations rather than conservation of energy. Clearly, the difficulties engendered by this approach were not realised at the time and the failure to reflect on the disconnection between the mathematics and the physics has left its mark on thermodynamics today. That leads inevitably to the question of what might usefully be taught in thermodynamics.

It is my own personal view that a fundamental revision of the foundations of the subject is required. Carnot was concerned with the reversibility of the cycle itself, which was also the view of Kelvin: the cycle can be performed in one direction to convert heat into work or in the other to convert work into heat. This view of thermodynamics has been overlooked in favour of Clausius, but the implication of the work summarised here is that this view is actually correct. There is a powerful argument, therefore, for returning to the origins of the subject and basing thermodynamics education not on entropy as a driving force or a determinant of equilibrium, but on cyclic processes. What, though, of entropy itself? If entropy is not a property of a body it must instead be associated with the flow of heat and the inequality of Eq. (11.1) has no meaning. Extending the First law to include changes in the number of particles and combining it with the Second Law would yield;

$$T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V - \eta\mathrm{d}N \tag{11.15}$$

Here, η represents the average energy of the particles.

This equation looks remarkably like the outcome of combining Eqs. (11.10) and (11.11), but is actually quite different. For the two systems considered in this chapter, this would give $T\mathrm{d}S = 0$ because entropy in this formulation is not associated with a property of a body but is solely the ratio of heat exchanged to the temperature at which it is exchanged. Given the widely accepted current view of entropy, this would appear to be a radical shift, but in fact it is consistent not only with energy conservation but the foundations of thermodynamics.

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References

Clausius R (1898) In: Hirst TA (ed) The mechanical theory of heat with its applications to the steam engine and to the physical properties of bodies. Taylor & Francis, London, p 215

Karam R (2014) Framing the structural role of mathematics in physics lectures: a case study on electromagnetism. Phys Rev Spec Top Phys Educ Res 10:010119

Landsberg PT (1961) Thermodynamics with quantum statistical illustrations. Interscience Publishers, New York

Magie WF (1899) The second law of thermodynamics: memoirs by Carnot, Clausius and Thomson. Harper Brothers, New York

Rebello NS, Zollman D, Allbough AR, Engelhardt PV, Gray KE, Hrepic Z, Itza-Ortiz SF (2005) Dynamic transfer. In: Mestre JP (ed) Transfer of learning from a modern multidisciplinary perspective. Information Age Publishing, Charlotte, NC

Redish EF, Gupta A (2010) Making meaning with math in physics: a semantic analysis. arXiv:1002.0472v1 [physics.ed-ph]

Zemansky MW (1968) Heat and thermodynamics, 5th edn. McGraw-Hill, New York