What, if anything, is entropy trying to tell us?

Rainer Müller

Technische Universität Braunschweig, Germany

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The notion of entropy is commonly regarded as one of the most challenging concepts in classical physics. Many learners have difficulties to develop an intuitive understanding of entropy as a physical concept. Some of the difficulties originate from the fact that in the thermodynamic definition of entropy dS = dQ/T, a state variable (entropy) is defined via a process variable (heat). The entropy definition of Lieb and Yngvason (1999) which is based on the concept of "adiabatic accessibility" has been a major advance in the foundations of thermodynamics. Unfortunately, because of its mathematical complexity, it is hardly accessible for students. We present a variant of this new entropy definition in an elementary formulation that should be accessible to undergraduate students. In this formulation, a direct link can be established to the idea of "quality of energy". With simple examples, we give an operational meaning to this term and point out how it is related to the traditional entropy definition.

Keywords: Entropy, Thermodynamics, Student Understanding

Introduction

Many students would agree that the notion of entropy is one of the most difficult in the entire physics curriculum. Indeed, a growing body of empirical research on student understanding indicates that entropy is a highly challenging concept for learners [1–5]. These findings immediately raise the question whether the traditional way of teaching entropy is the most appropriate one. Several authors [6-8] favour a microscopic approach to thermodynamics with a statistical interpretation of entropy. The "spreading and sharing of energy" [9-10] provides a physically satisfactory description of the second law at the microscopic level. Although the "spreading and sharing" approach has hardly been empirically tested, it certainly deserves a wider recognition than it has obtained until now.

This paper deals with the entropy concept in macroscopic thermodynamics. Here, the problems are even larger than in the microscopic approach. They may be traced back to a severe deficiency of the traditional definition of entropy. Entropy is a *state variable*. Like other state variables (e. g. temperature, pressure, or internal energy), it should represent a certain property of the state. There are not many students (or professional physicists, for that matter) who are able to give an adequate description what kind of property it is that is represented by entropy. The traditional approach does its best to hinder the appreciation of entropy as a property of a state because it defines entropy via the *process variable* heat. The entropy of a state B is defined by:

$$\Delta S_{AB} = \int_A^B \frac{dQ_{rev}}{T},\qquad(1)$$

where A is a reference state, and Q_{rev} is the heat transferred when going reversibly from A to B. Most textbooks merely show that the integral in (1) is independent of the path between A and B (so that entropy is a state variable) but do not give any further interpretation that would facilitate the comprehension of the new thermodynamic variable.

For the interpretation of entropy, we revive an old idea: Entropy measures the quality of energy. This view is commonly attributed to William Thomson (Lord Kelvin) but has never been formulated mathematically in a convincing manner. In this paper we show that the "quality" (or accessibility or usability) of energy is more than just a metaphor. With physical arguments and thought experiments, we can give a mathematical basis for this interpretation. The first and second law can then be formulated qualitatively in a simple and unified manner: The first law deals with the quantity of energy, while the second law describes the quality of energy. Remarkably, similar lines of reasoning show up in some early references [11, 12] but were apparently never pursued further.

Ordering of thermodynamic states

An essential element in our entropy definition is the fact that the equilibrium states of a system can be *ordered* according to their mutual *adiabatic accessibility*. This term belongs to an important strand of thought that was pioneered by Carathéodory [13], elaborated by Buchdahl [14], Falk and Jung [15], Giles [16], Landsberg [17], and Backhaus [18]. It culminated in the seminal 1999 paper of Lieb and Yngvason [19] which many consider the "last word" on entropy. A more accessible presentation of their ideas is given in [20].

The idea of adiabatic accessibility provides a means for *ordering* the states of a system. Entropy will later be defined so that the states ordered in this manner are arranged in the order of increasing entropy. At the moment, however, we do not assign a number S to a state. As an analogy, we can think of children which can be ordered according to their body size without actually quantifying their size with a meter stick.

Lieb and Yngvason [19] define adiabatic accessibility as follows: *"State A is adiabatically accessible from a state B, in symbols $A \prec B$, if it is possible to change the state from A to B by means of an interaction with some device (which may consist of mechanical and electrical parts as well as auxiliary thermodynamic systems) and a weight, in such a way that the device returns to its initial state at the end of the process whereas the weight may have changed its position in a gravitational field."*
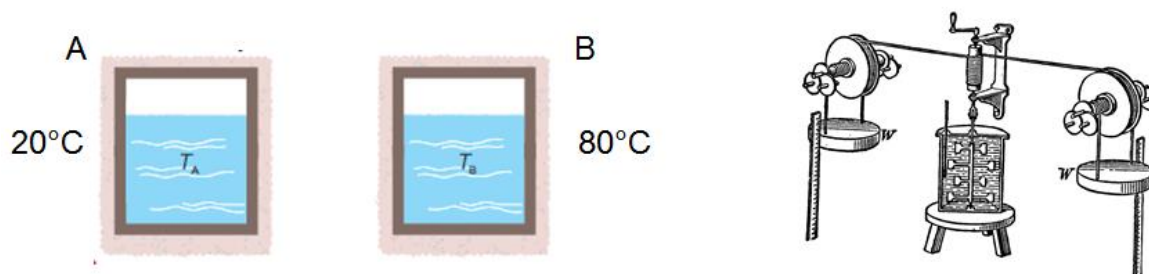

Fig.1: Joule's experiment as an example for adiabatic accessibility

The important point is that the transition from A to B has to be realized without the transfer of heat across the system boundaries – only raising or lowering a weight is allowed. Lieb and Yngvason show that all equilibrium states of a system can be ordered in this way. For any two states, one of the relations $A \prec B$ or $B \prec A$ always holds true. If both are true, the two states are said to be *adiabatically equivalent*. Two states of an ideal gas that are connected by a reversible adiabatic process ($p V^{\kappa}$ = const.) are an example of the latter case. The ordering induced by adiabatic accessibility is the first step towards entropy: $A \prec B$ implies $S(A) \leq S(B)$. If A and B are adiabatically equivalent, then, by definition, $S(A) = S(B)$.

Two examples

Let us illustrate the concept of adiabatic accessibility with two concrete examples. First consider a system that consists of a vessel with water. In state A, the temperature of the water is 20 °C, in state B it is 80 °C. It is easy to see that B is adiabatically accessible from A: By lowering a weight, the water in the vessel can be stirred so that the temperature rises (Joule's experiment; Fig. 1). On the contrary, nobody has ever found a way to "unstir" the water. It is an experimental fact that it is not possible to reach A from B without the transfer of heat across the system boundaries. Thus, we conclude that $A \prec B$ but not $B \prec A$ and consequently $S(A) < S(B)$.
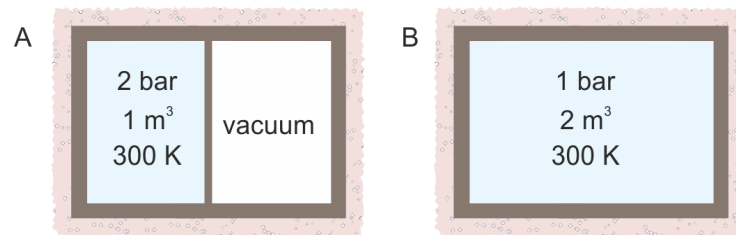

Fig. 2: Adiabatic accessibility in the free expansion of a gas

As a second example, consider an ideal gas in a box with a removable partition. The states A and B are defined as indicated in Fig. 2. Again, it is easy to adiabatically reach B from A: it is sufficient to remove the partition. However, it is impossible to go from B to A without transferring heat. The use of a piston does not help: Although it is possible to compress the gas adiabatically from 2 m^3 to 1 m^3, in this process the gas temperature will rise. Thus, even with the help of a piston, A cannot be reached from B without the transfer of heat. Again we conclude that $A \prec B$ but not $B \prec A$ so that $S(A) < S(B)$.
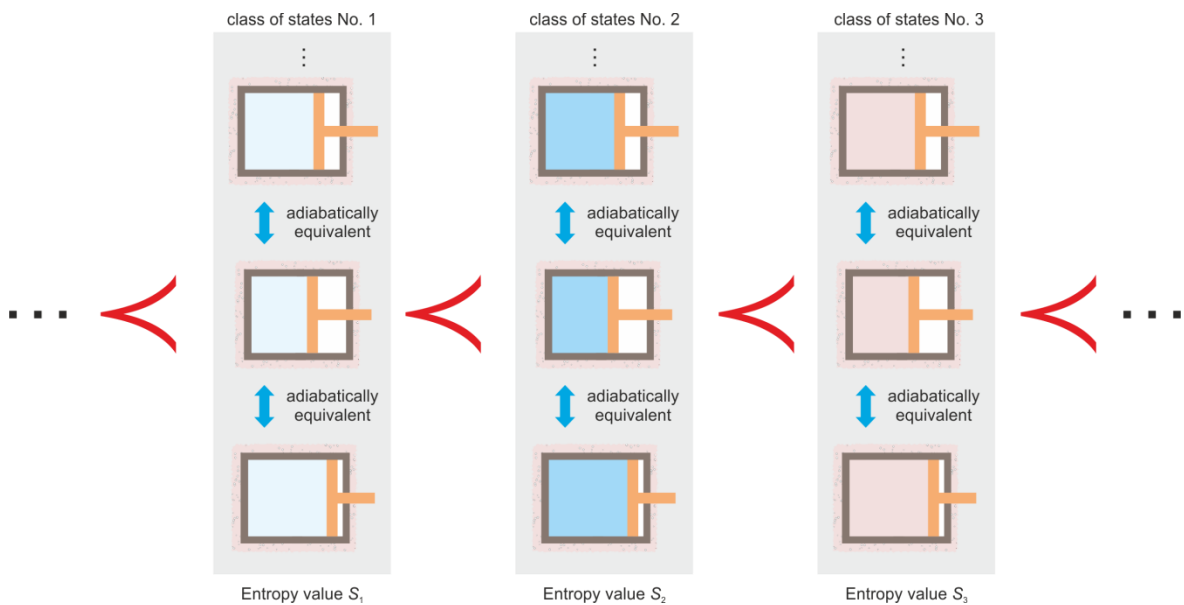

Fig. 3: Adiabatic accessibility defines an order relation for classes of system states. To each of the classes, an entropy value S can be assigned.

The quality of energy

The procedure outlined above defines classes of system states (Fig. 3). Within each class, the states are adiabatically equivalent (and thus have the same entropy [21]). The classes are ordered according to their relative adiabatic accessibility. The major part of our task is completed with this ordering of states. We only have to assign to any state a number S (the value of the entropy). To do this, we propose a different procedure than Lieb and Yngvason (who determine S by comparing the system in question with scaled copies of two reference systems). In order to facilitate the interpretation of entropy we base our definition on the idea of S representing the quality of energy (one could also use the terms usability or availability of energy). We define this term operationally by the ability to lift a weight as high as possible with a given amount of energy [22].

Let us illustrate the concept with a few examples:

1. Energy stored in a spring is "high-quality energy" – if 10 kJ of energy are stored in the system, all of it can be used to raise the weight with a suitable mechanism.

2. Energy stored in an adiabatically compressed gas is high-quality energy, too. In a reversible adiabatic compression of the gas, all of the work is stored as internal energy, while the temperature of the gas rises. The stored energy can be completely retrieved by the reverse process. This example shows that – contrary to a common belief – "thermal energy" is not *per se* low-quality energy.

3. Heated water in a thermally isolated vessel is an example of lower-quality energy. If the internal energy of the water is increased by 10 kJ (e. g. with an electric heater), it is not possible to use this energy completely for doing work. Even with a heat engine, it is not possible to lift the weight to the same height as in the case of the spring or the compressed gas. The height to which the weight can be lifted depends on a variety of variables, including the temperature of the environment.

In order to describe the "quality of energy" quantitatively, we have to find a way to relate the operational procedure outlined above to the state variables of the system. From the examples we see that it is reasonable to consider *finite* systems – it doesn't make much sense to ask how high a weight can be raised with the energy stored in an infinite system.
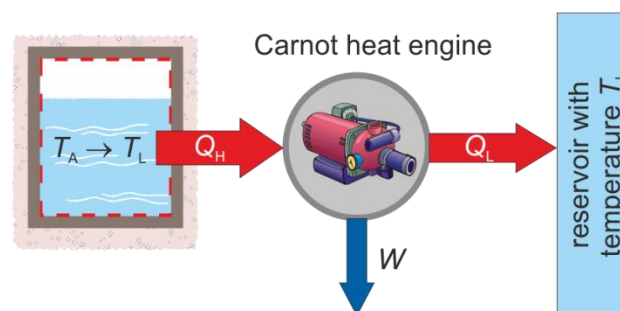

Fig. 4: Heat engine with a finite source

Digression: Heat engine with a finite source

Let us analyse Example 3 in more detail. Consider the situation shown in Fig. 4. A vessel is filled with water of temperature T_A. The water is used as the high-temperature "reservoir" of a Carnot heat engine. The temperature of the infinitely large low-temperature reservoir is T_L. Because the amount of water in the vessel is finite, it cools down while driving

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the Carnot engine. The engine ceases to work when the water has cooled to the temperature T_L. We ask: What is the total work output of the Carnot engine while the water in the vessel cools down from T_A to T_L?

We consider a small portion of the process in which the temperature of the water can be assumed to have a constant temperature T. The portion of the process should comprise an integral number of cycles of the Carnot engine. The work extracted is related to the heat ΔQ_H delivered by the water via the Carnot efficiency η_{Carnot}:

$$\Delta W = -\eta_{Carnot} \cdot \Delta Q_H = -\left(1 - \frac{T_L}{T}\right) \cdot \Delta Q_H. \tag{2}$$

While the water gives off the heat ΔQ_H, its temperature changes by ΔT according to $\Delta Q_H = c\,m\,\Delta T$, where m is the mass and c the heat capacity of the water. Eq.(2) becomes:

$$\Delta W = -\eta_{Carnot} \cdot \Delta Q_H = -\left(1 - \frac{T_L}{T}\right) \cdot c \cdot m \cdot \Delta T. \tag{3}$$

The total amount of work done by the Carnot engine while the water cools down is obtained by integrating from T_A to T_L:

$$W_{A \to L} = -\int_{T_A}^{T_L} \left(1 - \frac{T_L}{T}\right) \cdot c \cdot m \, dT. \tag{4}$$

We obtain:

$$W_{A \to L} = \Delta U - T_L \cdot \int_{T_L}^{T_A} c \cdot m \frac{dT}{T}, \tag{5}$$

where $\Delta U = c\,m\,(T_A - T_L)$ is the difference of the internal energies in the initial and final state of the water. Eq. (5) can be readily interpreted: ΔU is the total energy "stored" in the water. Even with a heat engine, not all of it can be used to do work. The second term is the "unavailable energy" [23] (often called *anergy*). The percentage of the energy that cannot be used depends not only on the initial temperature of the water but also on the temperature of the environment.

In a more rigorous formulation of the above argument, one would not take for granted that the Carnot efficiency is the maximal heat engine efficiency. Instead one would refer more abstractly to the largest elevation of the weight that can be achieved by any conceivable device under the specified conditions. Eq. (5) thus has the character of an empirical law.

Quality of energy: Incompressible substance

To clarify the concept of quality of energy let us first illustrate what we have *not* in mind. Consider again the two vessels of water shown in Fig. 1. Ask an engineer which of the two is more valuable for the purpose of doing work. Of course he will choose the one with the higher temperature (which also has a higher U). The engineer's answer is simply a matter of *quantity* (which is governed by the first law). However, the quantity of energy is not our aim – we are interested in *quality*. The question we have asked was too simple.

We have to modify our question slightly to aim at the quality of energy. For the moment, we restrict ourselves to incompressible systems (i. e. liquids or solids). To get rid of any first-law issues, we only compare systems with the same mass and the *same total energy*.
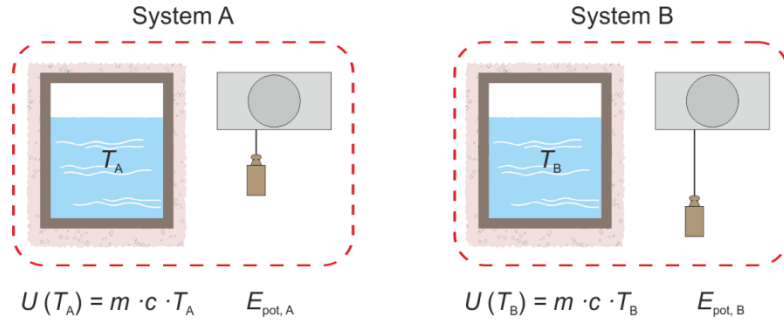
Fig. 5: Comparing systems at constant total energy

Each system is equipped with a weight (Fig. 5) which is adjusted so that for all systems under consideration, the sum of internal and potential energy is the same:

$$E_{\text{total}} = U(T_{\text{A}}) + E_{\text{pot, A}} = U(T_{\text{B}}) + E_{\text{pot, B}}. \tag{6}$$

Again we ask: Which of the two systems is more valuable for doing work? Now the engineer's answer will be different. To extract work from the system, he can now (a) lower the weight and (b) cool down the vessel to the environment temperature T_{L} with Carnot efficiency. The sum of both contributions has to be compared to assess the quality of the energy stored within each system. While the potential energy of the weight is fully usable, the maximal work output from cooling down the vessel is given by Eq. (5). Adding both contributions, we obtain for system A:

$$W_{\max}(\text{A}) = E_{\text{pot, A}} + W_{\text{A}\rightarrow\text{L}}$$
$$= E_{\text{total}} - \cancel{U(T_{\text{A}})} + \cancel{U(T_{\text{A}})} - U(T_{\text{L}}) - T_{\text{L}} \cdot \int_{T_{\text{L}}}^{T_{\text{A}}} c \cdot m \frac{\text{d}T}{T}. \tag{7}$$

An analogous expression is obtained for system B. Eq. (7) does not look very helpful, because $W_{\max}(\text{A})$ depends on the environment temperature and on the total energy E_{tot} which can be arbitrarily chosen. It is remarkable, however, that the combination

$$\Delta S_{\text{AB}} = \frac{W_{\max}(\text{A}) - W_{\max}(\text{B})}{T_{\text{L}}} = \int_{T_{\text{A}}}^{T_{\text{B}}} c \cdot m \frac{\text{d}T}{T} \tag{8}$$

is independent of both. It depends only on the properties of the two states A and B. Thus, it can serve as a measure for comparing the quality of the energy in the two systems. We define the entropy difference for two states of an incompressible substance by Eq. (8). Note that with $\text{d}Q = c \cdot m \cdot \text{d}T$, this equation can be written in the traditional form:

$$\Delta S_{\text{AB}} = \int_{T_{\text{A}}}^{T_{\text{B}}} \frac{\text{d}Q}{T}. \tag{9}$$

Defining entropy in general

If we had to deal only with incompressible substances, Eq. (8) would give a satisfactory definition of entropy. However, the whole argument breaks down for gases (or generally, for systems with variable volume). The interpretation of Eq. (8), which rests on comparing the maximal amount of obtainable work, becomes less straightforward if additional work can be done by changing the volume.
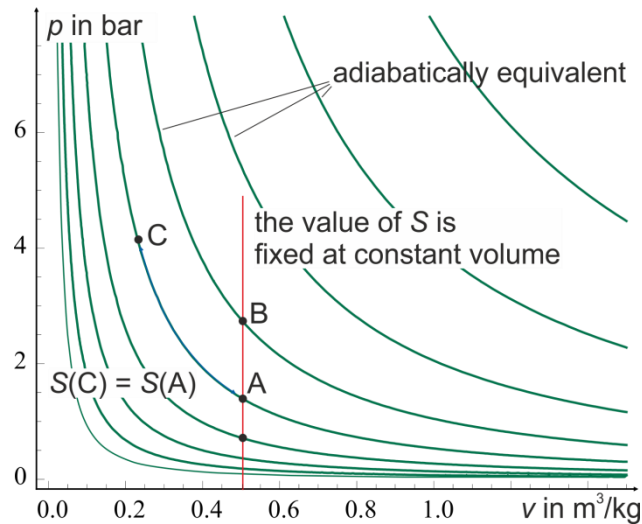
Fig. 6: Defining entropy: Example of an ideal gas

At this point, we have to return to the ordering attained by adiabatic accessibility. To be more specific, we consider the case of an ideal gas (Fig. 6). Adiabatic curves (pV^κ = const.) are shown in green. All states on the same adiabatic curve are adiabatically equivalent and thus have the same entropy. For example: $S(C) = S(A)$. The adiabatic curves represent the equivalence classes of states shown in Fig. 3.

The crucial point is: It is sufficient to analyze just one state in order to determine the numerical value of S for the whole equivalence class. This observation completes our definition of entropy because with Eq. (8), we can compare two states with the same value of V (red line in Fig. 6) and calculate their entropy difference. In this way, a numerical value of S can be attributed to all states belonging to the corresponding equivalence class.

Thus, in order to calculate the entropy difference of the two states B and C in Fig. 6, we identify the state A which is adiabatically equivalent to C and has the same volume as B. The entropy difference ΔS_{AB} can be determined with Eq. (8), while A and C have the same entropy. Because, by definition, A and C are connected by an adiabatic process ($Q = 0$), we arrive at the well-known formula:

$$\Delta S_{CB} = \int_{T_C}^{T_B} \frac{dQ}{T}. \tag{10}$$

The argument not only holds for gases, but for simple thermodynamic systems in general. It is not necessary to prove that the integral in Eq. (10) is path independent so that S is a state variable. This result is guaranteed by the existence of an order relation because the position of the state within the order is already a property of the state. Eq. (10) just quantifies this property.

Conclusion

We have shown that entropy can be interpreted as the quality of energy by giving an operational definition that leads to the same mathematical expression as the traditional approach. We hope that this line of reasoning makes it easier for students to develop an intuitive feeling for this central concept in thermodynamics. We do not pretend that by using our approach, entropy suddenly becomes an "easy" subject. However, students can now assign a physical interpretation to an otherwise fairly abstract concept. We are planning empirical

studies that will show whether the approach proposed in this paper leads to an improved understanding of thermodynamics.

With the "quality of energy" approach, not only the definition of entropy but also the second law can be consistently interpreted. Entropy is a non-conserved quantity: It can cross the system boundaries, but it can also be created by irreversible processes within the system. The generation of entropy corresponds to lowering the quality of the system's energy. Often, the term "degradation of energy" is used to describe this process. Thus, our interpretation of entropy facilitates a discussion of the second law that focuses on this aspect.

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[21] More precisely, adiabatic accessibility orders the states according to their entropy per unit mass or specific entropy $s = S/m$.

[22] For brevity, we use the term "work" to denote energy that can be used to lift a weight. It is known that many students have difficulties with the concept of work. Alternative expressions would be "available energy" or "generally usable energy".

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