André Thess

The Entropy Principle

THERMODYNAMICS FOR THE UNSATISFIED

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With 55 Figures and 4 Tables

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Temperature … is a corollary of entropy;
it is epilogue rather than prologue.

Elliott Lieb, Jakob Yngvason

Preface

Is it possible to define entropy in classical thermodynamics in a way that is mathematically accurate and at the same time easy to understand? I have often asked this question to myself first when I was a student and later when I became a professor of mechanical engineering and had to teach thermodynamics. Unfortunately, I never got a satisfactory answer. In textbooks for physicists I often found the claim that entropy can only be "really" understood when one has recourse to statistical physics. But it appeared strange to me that a physical law as perfect as the second law of thermodynamics, which is closely related to entropy, should depend on tiny details of the molecular structure of the matter that surrounds us. By contrast, in textbooks for engineers entropy was most often defined on the basis of temperature and heat. However, I never felt comfortable with the idea that such a fundamental quantity as entropy should be determined on the basis of two concepts which cannot be accurately defined without entropy. Given this state of affairs, I came close to resignation and was on the verge of believing that an accurate and logically consistent definition of entropy in the framework of a macroscopic theory was altogether impossible.

In the spring of the year 2000, I came across an article entitled "A Fresh Look at Entropy and the Second Law of Thermodynamics" written by the physicists Elliott Lieb and Jakob Yngvason which appeared in the journal *Physics Today*. Their idea that the concept of adiabatic accessibility rather than temperature or heat is the logical basis of thermodynamics appealed to me immediately. For the first time in my academic life I began to feel that I really understood the entropy of classical thermodynamics. However, it took considerable effort to study and understand the article "The Physics and Mathematics of the Second Law of Thermodynamics" (*Physics Reports*, vol. 310, 1999, pp. 1–96) by the same authors in which the full "Lieb-Yngvason theory" is presented. Once I had finished the work, however, I was convinced that the Lieb-Yngvason theory represents the ultimate formulation of classical thermodynamics. Although the theory is mathematically complex, it is based on an idea so simple that each student of science or engineering should be able to understand it.

I then decided to involve my students in order to test whether the Lieb-Yngvason theory is as convincing as I believed. I have been teaching a one-year thermodynamics course for the undergraduate mechanical engineering students of Ilmenau University of Technology since 1998. I use Moran and Shapiro's textbook "Fundamentals of Engineering Thermodynamics" (Wiley and Sons), and I introduce entropy as is currently most often done in engineering courses, namely via the Carnot process cycle and the Clausius inequality. One week after having introduced entropy in the regular lecture, I invited the students to a voluntary 90-minute supplementary lecture and presented them with the basic ideas of the Lieb-Yngvason theory. I was prepared for the worst-case scenario and predicted that the roughly sixty students who showed up would shower me with a torrent of rotten eggs and tomatoes after being confronted with my presentation of this complex mathematical apparatus. Surprisingly, the opposite happened. In an anonymous questionnaire that I distributed after the lecture, more than two-thirds of the students stated that they found the definition of entropy according to the Lieb-Yngvason theory more plausible than the traditional one. Some even asked me if I could incorporate the Lieb-Yngvason theory into my regular thermodynamics course.

Such an encouraging response prompted me to extend and write up my lecture notes in order to make Lieb and Yngvason's work accessible to a broader readership. This book is intended as supplementary material to existing textbooks of thermodynamics and is primarily written for those students who find the traditional definitions of entropy unsatisfactory. Accordingly, the contents of the book do not constitute a self-contained introduction to thermodynamics. It is rather suited as a short course on the accurate formulation of classical thermodynamics whose content can be adjusted to the time and interests of the students. In my experience, the minimal version of a supplementary short course consists in a single lecture lasting 90 to 120 minutes which is presented in addition to the regular thermodynamics course. In this time, the lecturer can cover the basic ideas of Chap. 1, 2 and 3. However, in later years it turned out to be more appropriate to use two or three hours. The first half of the time can be devoted to the fundamentals explained in Chap. 1–3. During the second part, Chap. 4 as well as one or two selected examples from Chap. 5 can be covered.

I hope that this book conveys some of the fascination that I experienced when studying the Lieb-Yngvason theory. I would like to emphasize that I have made no contribution to the formulation of the theory presented here. My only task was to translate the mathematically complex theory into the language of undergraduate science and engineering students. Accordingly, I take the responsibility for all errors or misrepresentations of the original theory. The Lieb-Yngvason theory itself, I believe, is perfect.

It is my pleasure to express my gratitude to Elliott Lieb and Jakob Yngvason for answering many questions and encouraging me to write this book as well as prepare an English version. Moreover, I would like to thank Friedrich Busse, Gerhard Diener, Walter John and Holger Martin for valuable suggestions and useful discussions. I also thank Rainer Feistel, Achim Dittmann, Andreas Pfennig and Roland Span for their help with thermodynamic data. Finally, my thanks go to Cornelia Gießler, Martina Klein and Renate Heß for their help in preparing the figures and to Armin Stasch, scientific book designer, for his invaluable help with typesetting.

The authors and the date of origin of the Holy Bible are unfortunately unknown. For the bible of classical thermodynamics, however, this information is readily available: It was written by Elliott Lieb and Jakob Yngvason, it carries the title "The Physics and Mathematics of the Second Law of Thermodynamics" and it was first published in 1999 in the journal *Physics Reports*. I hope that this book will encourage its readers to study the bible of thermodynamics!

André Thess
Ilmenau, 18 January 2010

Contents

Chapter 1 Introduction

Introduction

1.1 Is Entropy Really Necessary?

Why does a glacier flow? Why does a diver die when he rises too quickly to the surface of the water? Why does salt pull the water out of a cucumber? Why does a warm bottle of soda produce more foam upon opening than a cold one? Why is it impossible to use the heat of the Gulf Stream for the production of electricity? All these questions have one property in common: they cannot be answered without considering entropy.

Temperature, pressure and volume are quantities of which we have a sound intuitive understanding. Internal energy U, whose existence is postulated by the first law of thermodynamics, is slightly more difficult to comprehend. Yet everyone becomes familiar with this quantity after solving a couple of textbook problems. But how about entropy? Many people confess that they have never understood the real meaning of this intriguing quantity. Do we need it at all? Can't we do thermodynamics without struggeling with entropy? Are the foregoing quantities not sufficient to solve all practical thermodynamic problems?

A simple example shows us that this is not the case. When a stone falls into a well, the energy of the water increases by the same amount as the decrease in potential energy of the stone. Can this process run spontaneously in the reverse direction? It would certainly not violate the first law of thermodynamics if water would spontaneously cool down a little bit and conspire to throw a stone into the sky. Nevertheless, our experience shows that such a process doesn't ever occur. Our physical intuition suggests that "something" has been lost in the system consisting of the water and the stone once the stone has fallen down. In what follows we will see that this "something" can be accurately described in mathematical terms and leads us to the concept of entropy. Thanks to a recent work by the physicists Elliott Lieb and Jakob Yngvason (Lieb and Yngvason 1999), we will be able to give a definition of entropy which is characterized by unprecedented mathematical and logical rigor. The purpose of this book is to make this "Lieb-Yngvason theory" accessible to undergraduate students as well as to other scientists and engineers interested in the fundamentals of thermodynamics.

The logical chain of arguments that lead us to entropy starts with the order relation

$$\prec \tag{1.1}$$

called adiabatic accessibility. The overarching goal of the present book is to understand how entropy can be derived from this fundamental concept. To give the reader a first glance at the result, the entropy S of the state X of a thermodynamic system is given by the relation

$$S(X) = \max\{\lambda : ((1-\lambda)X_0, \lambda X_1) \prec X\} \quad (1.2)$$

This definition is awkward, as it contains unusual symbols and does not appeal to our intuition. Few readers, if any, will find that something has been gained by replacing a seemingly clear definition like $\mathrm{d}S = \delta Q / T$ (which can be found in many textbooks of thermodynamics) by Eq. 1.2. However, it turns out that Eq. 1.2 is only slightly more complicated than the formula

$$W(X) = \min\{\lambda : \lambda Y_0 \prec X\} \quad (1.3)$$

defining the value W of an object X in the fairy tale "Hans in Luck". Let us turn to this popular piece of German literature, written by the brothers Grimm, in order to acquire the mathematical tools necessary to understand entropy.

1.2 A Didactic Model for the Logical Structure of the Entropy Principle

> Hans had served his master for seven years. When he left, his master gave him a piece of gold in reward for his work. Soon after, when Hans set out on his way home, the gold started to hurt his shoulder. He was happy to find a horseman who gave him his horse in exchange for the gold. But the horse threw him off, so he gave it away for a cow, the cow for a pig, the pig for a goose and the goose for a grindstone. When he stopped at a well in a field to refresh himself, he slipped and fell, pushing against the grindstone so that it fell into the water. He thanked God for having delivered him in such a good way from these heavy burdens which had been the only things that troubled him. "There is no man under the sun so fortunate as I" he cried out. With a light heart and freedom from every burden he now ran uninhibited until he arrived home where his mother was waiting.

The full fairy tale is given in the Appendix A.

Parents read this fairy tale to their children in order to teach them that each object has a value and that this value can be irrevocably destroyed by careless action. The parents could equally well show Eq. 1.3 to their children but this is unlikely to be a good idea. We, however, would like to use the (incomplete) analogy between the value W in Grimm's fairy tale and the entropy S in physics to convince ourselves that entropy is not as difficult to understand as Eq. 1.2 might suggest. The logic behind the derivation of entropy in Chap. 2 and 3 will turn out to be similar to the definition of the value in the present chapter.

Let us denote Hans' property by the symbol X, which stands for G (gold), H (horse), C (cow), P (pig), B (goose – with B from bird), S (grindstone – with S from stone), O (nothing). In addition we shall assume that Hans could have exchanged the piece of gold for a house R (with R from residence) and could have reversed this deal at any time. We now define financial accessibility as a basis for understanding adiabatic accessibility in Chap. 2.

> **Financial accessibility.** An object Y is financially accessible from an object X, denoted $X \prec Y$ (pronounced "X precedes Y"), if there is a market in which it is possible to exchange X for Y.

In our example we obviously have $G \prec H$, $H \prec C$, $C \prec P$, $P \prec B$, $B \prec S$, $S \prec O$. Since we have made the additional assumption that Hans could have exchanged his wages for a house R and the house back for the gold, both $G \prec R$ and $G \succ R$ (pronounced "G succedes R") must hold. We shall denote two objects which are mutually financially accessible as *financially equilvalent*, and write $G \stackrel{E}{\sim} R$. If Y is accessible from X but the converse is not true, we shall write $X \prec\prec Y$ (pronounced "X strongly precedes Y"). In our fairy tale, there is $G \prec\prec H$, $H \prec\prec C$, $C \prec\prec P$ and so on. We further assume that a spontaneous gain which would correspond to exchanging a grindstone for a piece of gold is impossible. An important property of the relation $\prec$ should be particularly emphasized. The decision whether the statement $X \prec Y$ is true is a binary decision. This means that the answer to the question "Is $X \prec Y$ true?" must be either **YES** or **NO**. Consequently, the information about the financial accessibility of a given set of objects can be represented by a table with binary entries.

a

	G	H	C	P	B	S	0	R
G	Y	Y	Y	Y	Y	Y	Y	Y
H	N	Y	Y	Y	Y	Y	Y	N
C	N	N	Y	Y	Y	Y	Y	N
P	N	N	N	Y	Y	Y	Y	N
B	N	N	N	N	Y	Y	Y	N
S	N	N	N	N	N	Y	Y	N
0	N	N	N	N	N	N	Y	N
R	Y	Y	Y	Y	Y	Y	Y	Y

b

W(G) = 1
W(H) = 0.8
W(C) = 0.7
W(P) = 0.5
W(B) = 0.3
W(S) = 0.2
W(0) = 0
W(R) = 1

Fig. 1.1. *Hans in Luck and the value principle.* Illustration of the financial accessibility (a) and the hypothetic value (b) of objects in the brothers Grimm's fairy tale "Hans in Luck". The abbreviations denote gold (G), horse (H), cow (C), pig (P), goose (B) (like **b**ird), grindstone (S), and nothing (0). For illustrative purposes, an additional object has been introduced, a house (R) (like **r**esidence), which is not present in the fairy tale. In table (a) **Y** and **N** denote respectively **YES** and **NO** as answers to the question whether an object in the first line of the table is financially accessible from an object in the first column. For instance, the response to the question "Is $G \prec S$ true?" is **YES** (line 2, column 7), whereas the answer to "Is $S \prec G$ true?" is **NO** (line 7, column 2). The units of the values in (b) are arbitrary. The numbers do not have a particular meaning except that they roughly reflect the order of the values of the considered objects

Figure 1.1 shows the result that we would have obtained if we had checked the financial accessibility of all objects occurring in "Hans in Luck". Although our example contains as little as eight different objects, the table is already quite large. Is it possible to represent the contents of this table in a more concise manner? This is indeed the case if we introduce the notion of *value*. Figure 1b shows one of many possibilities of assigning to each object X a value $W(X)$. The information content of both tables is the same. However, Fig. 1b is much more compact than Fig. 1a. If we wish to know whether Y is financially accessible from X we only need to compare the values $W(X)$ and $W(Y)$. If $W(X) > W(Y)$, then $X \prec\prec Y$, whereas if $W(X) < W(Y)$, then $X \succ\succ Y$. Finally if $W(X) = W(Y)$, then obviously $X \prec Y$ and $X \succ Y$ and thus $X \stackrel{E}{\sim} Y$. The conclusion that the relation $\prec$ of financial accessibility between different objects can be completely described – or encoded – by a function $W(X)$ can be mathematically expressed in the following way.

Value principle. There is a real valued function on all objects X called value and denoted by W such that:

- Monotonicity: If $X \prec\prec Y$ then $W(X) > W(Y)$, if $X \stackrel{E}{\sim} Y$ then $W(X) = W(Y)$
- Additivity: $W((X, Y)) = W(X) + W(Y)$

In contrast to the entropy principle discussed in later chapters, the value principle should not be considered as a rigorous mathematical result but rather as an illustrative informal example. It can be readily verified that the values given in Fig. 1b satisfy these properties. The monotonicity ensures that two objects are financially equivalent if their values are equal and that a series of careless exchanges with $X \prec\prec Y$ and $Y \prec\prec Z$ is equivalent to a continuous degradation of values with $W(X) > W(Y) > W(Z)$. Additivity implies that the value of a compound system (X, Y), i.e., a system which contains two objects X and Y, is equal to the sum of the individual values. This property seems trivial. But this is not the case. Indeed, additivity of W has far-reaching consequences. For instance, additivity implies that states are financially accessible for a compound system which is not financially accessible for a single object. To give an example, two geese ($Y = 2B$) are financially inaccessible from one goose ($X = 1B$) because $W(1B) < W(2B)$. If, however, we have additional resources at our disposal, – for instance two pieces of gold, – then the compound system $(1B, 2G)$ can financially access the compound system $(2B, 1G)$ because the value $W(1B, 2G) = 2.3$ of the former exceeds the value $W(2B, 1G) = 1.6$ of the latter. The additivity, like an invisible band, connects objects with entirely different properties. A haircut and a hamburger have very little in common, except that both have a certain value.

After having acquainted ourselves with the properties of the function $W(X)$, we turn to the question how to determine it. In the first step, we choose an arbitrary good Y_0 as a reference object. For instance, a piece of gold with a mass of one kilogram could serve as such an object. In the second step, we introduce a scaling factor λ and denote λY_0 as a *scaled copy* of Y_0. In our example $\lambda = 0.3$ corresponds to 300 grams of gold. In a third and final step we define the value of an object as the minimum of λ for which the quantity λY_0 of gold is sufficient in order to financially access the object. The mathematical expression of this definition is

$$W(X) = \min\{\lambda : \lambda Y_0 \prec X\} \tag{1.4}$$

This definition should be pronounced as follows: "The value of X is equal to the minimum of λ which has the property that X is financially accessible from λY_0." The so-defined value is dimensionless. If $\lambda = 2$ holds for an object, then its value is equal to the value of two kilograms of gold. In practice, however, we use dimensional values. We transform $W(X)$ into a dimensional quantity by allocating a unit, say 10 000 €, to the reference object. We then obtain the dimensional value as

$$W_*(X) = W(X) \times 10000\,€ \tag{1.5}$$

Thus, the determination of the value according to the Definition 1.4 is reduced to a series of experiments, each of which yields a yes-or-no answer. In our example, we could determine the value in two ways by approaching the minimum of λ either from below or from above. A generous person would first exchange one kilogram of gold ($\lambda = 1$) for a goose, notwithstanding the horrendous financial loss associated with this transaction. She or he would then repeat the experiment by decreasing the amount of gold in steps of, say, one gram. The 702$^{\text{th}}$ experiment (question: "$0.299\,Y_0 \prec X$?", answer: "**NO**!") would be unsuccessful and thus the value would have been determined as $W = 0.3$. Conversely, a mean person would start with one gram of gold ($\lambda = 0.001$). After 299 unsuccessful attempts to exchange amounts of gold increasing in steps of one gram, the affirmative answer to the question "$0.3\,Y_0 \prec X$?" would lead him or her to the conclusion that $W = 0.3$. We thus realize that the value of an object can be determined in a strictly deterministic way. Equipped with such a profound understanding of German literature we can summarize our findings in the following sentence (which should not be taken too seriously).

> **Principle of value decrease.** In the hands of a fool property will never increase its value, i.e., $\Delta W \leq 0$.

With this statement, we finish our discussion of the didactical model which should be considered as an informal introduction rather than a rigorous mathematical theory. In order to prepare ourselves for the return to thermodynamics, we summarize our conclusions regarding financial accessibility and value in the following compact form.

1. Objects can be sorted using the order relation $\prec$, which we denote as financial accessibility;
2. The object Y is said to be financially accessible from the object X, written $X \prec Y$, if there is a market in which X can be exchanged for Y;
3. Our everyday experience about the financial accessibility of objects can be summarized in the form of the following value principle.
4. **Value principle.** There is a real valued function on all objects X called value and denoted by W such that W is monotonic [if $X \prec\prec Y$ then $W(X) > W(Y)$, if $X \overset{E}{\sim} Y$ then $W(X) = W(Y)$] and additive [$W((X, Y)) = W(X) + W(Y)$].

Before turning to the following chapter it is instructive to take a quick look at the summary of the whole book which is given in Chap. 6. This will lead us to the conclusion that with our introductory example we have already made a great step towards understanding the entropy principle. Ahead of us is a lot of technical work, but the logic behind this work will be very similar to what we have just learned.

Chapter 2 Adiabatic Accessibility

Adiabatic Accessibility

2.1 Thermodynamic Systems

Thermodynamics is the science of the transition of thermodynamic systems between different equilibrium states and the associated changes of their energy and chemical composition. A thermodynamic system is a well-defined quantity of matter which is scalable and which can exchange energy with its environment. Examples of thermodynamic systems are 1 kg of ice, 500 g of alcohol, 450 g of red wine or 1 mole of sulfuric acid. *Scalability* refers to the possibility of splitting the system into several parts without changing the properties or recombining several systems into a larger one. For instance, we can divide 450 g of red wine among three glasses with 150 g each without changing the properties of the wine. By contrast, a single molecule does not constitute a thermodynamic system because it lacks the property of scalability. Indeed, if we let two molecules react and form one large molecule, the properties of the latter will be different from its constituents. Our Universe is not a thermodynamic system either, since its division or duplication is unlikely to make physical sense. Complex systems like humans or animals do not represent thermodynamic systems either, because it is not possible to split them into living small sub-individuals. Neither is it possible to combine one million mice to create a single giant living mouse. In summary, a thermodynamic system should be neither too small nor too large or complex.

2.2 Equilibrium States

Classical thermodynamics deals with systems that are in the state of thermodynamic equilibrium. These states will be referred to as equilibrium states or simply *states*. We shall define them as follows.

> **Equilibrium states** (physical definition). A thermodynamic system is said to be in an equilibrium state if its properties are stable in time and can be described by a small number of macroscopic quantities.

The exploding boiler of a steam locomotive, for instance, is not in a thermodynamic equilibrium state because the process proceeds very fast and the number of data necessary to specify the details of the instantaneous motion of the two-phase mixture and the debris is huge. By contrast, 500 grams of Vodka in a refrigerator is very close to an