HANS U. FUCHS

THE DYNAMICS OF HEAT

热动力学

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Preface

The last few decades have seen the development of a general approach to thermodynamic theory. Continuum thermodynamics has demonstrated to us how we can build a theory of the dynamics of heat rather than of statics. In this book I would like to transfer what I have learned about the general theory to an introductory level and to applications in the sciences and engineering.

Two elements combine to make this presentation of thermodynamics distinct. First of all, taking as the foundation the fundamental ideas that have been developed in continuum thermodynamics allows one to combine the classical theory of thermodynamics and the theory of heat transfer into a single edifice. Second, didactic tools have been built that make it not just simple, but rather natural and inevitable to use entropy as the thermal quantity with which to start the exposition. The outcome is a course that is both fundamental and geared toward applications in engineering and the sciences.

In continuum physics an intuitive and unified view of physical processes has evolved: That it is the flow and the balance of certain physical quantities such as mass, momentum, and entropy which govern all interactions. The fundamental laws of balance must be accompanied by proper constitutive relations for the fluxes and other variables. Together, these laws make it possible to describe continuous processes occurring in space and time. The image developed here lends itself to a presentation of introductory material simple enough for the beginner while providing the foundations upon which advanced courses may be built in a straightforward manner. Entropy is understood as the everyday concept of heat, a concept that can be turned into a physical quantity comparable to electrical charge or momentum. With the recognition that heat (entropy) can be created, the law of balance of heat, i.e., the most general form of the second law of thermodynamics, is at the fingertips of the student.

The book contains two lines of development which you can either combine (by reading the chapters in the sequence presented) or read separately. In addition to the four chapters which represent the main line, you will find a Prologue, an Interlude, and an Epilogue which discuss some subjects at a somewhat higher level.

The four chapters that form the main body of the text grew out of my experience in teaching thermodynamics as a part of introductory physics, but represent an extension both in content and level of what I commonly include in those courses. The extension mostly concerns subject matter treated in courses on engineering thermodynamics and heat transfer and applications to solar energy engineering. Still, the chapters maintain the style of a first introduction to the subject. Previous knowledge of thermal physics is not required, but you should be familiar with basic electricity, mechanics, and chemistry, as they are taught in introductory college courses. With the exception of one or two subjects, only a modest amount of calculus is used. Chapter 1 provides an introduction to basic quantities, concepts, and laws. Entropy is introduced as the quantity which is responsible for making bodies warm or for letting ice melt, and the law of balance of entropy is formulated directly on the basis of ideas taken from everyday images of heat. The relation between currents of heat (entropy) and currents of energy is motivated along the lines of Carnot's theory of heat engines, yielding a law which makes the development of thermodynamics rather simple. (The relation is proved later on the basis of some alternative assumptions in the Interlude.) Then, some simple applications which do not rely too heavily upon particular constitutive relations are developed. First among them is a treatment of irreversibility and the loss of power in thermal engines, a subject which teaches us about the importance of the rule of minimal production of heat. Chapters 2, 3, and 4 furnish introductions to constitutive theories. The first of these deals with uniform bodies, which respond to heating by changing mechanical or other variables. A simple version of the constitutive theory of the ideal gas is developed, which leads to a theory of the thermodynamics of ideal fluids. In addition, blackbody radiation and magnetic bodies are treated. A short exposition of the concepts of thermostatics exposes the reader to the difference between dynamics and statics in the field of thermal physics. Chapter 3 deals with theories of heat transfer excluding convection. The general form of the equation of balance of entropy for bodies and control systems is given and applied to various cases. Production rates of heat in conduction and radiation are calculated and applied, among others, to the computation of the maximum power of solar thermal engines. In this chapter, continuous processes are treated for the first time in the context of one-dimensional conduction of heat. The radiation field and the issue of the entropy of radiation are discussed extensively, and a section on solar radiation concludes this Chapter. Chapter 4 extends the theory of heat to processes involving the change and the transport of substances. Subjects such as chemical reactions, phase changes, and convection, and applications to power engineering and to heat exchangers form the body of this Chapter. All of these Chapters include a large number of solved examples in the text.

The second track of the book treats thermodynamics in a more advanced and formal manner. The Prologue provides a brief view of a unified approach to classical physics. Except for the first section, which you definitely should read before starting with Chapters 1 - 4, the Prologue presents several subjects of physics at a relatively quick pace, demonstrating the unified approach to dynamical processes which forms the backbone of the entire book. (The concepts are introduced at a more leisurely pace in the main chapters on thermodynamics.) If you wish, you can then try to read the Interlude which introduces the subject of the thermodynamics of uniform fluids on the basis of the caloric theory of heat. This Chapter repeats the subject of part of Chapter 1 and most of Chapter 2 at a higher mathematical level. In contrast to those chapters, the Interlude also provides a first proof of the relation between currents of entropy and of energy, which shows that the ideal gas temperature can be taken as the thermal potential. Finally, the Epilogue takes the first simple steps into the field of continuum thermodynamics, exposing you to the ideas behind the more advanced subjects which have been the focus of development over the last few decades.

If I seem to succeed in introducing you to an exciting new view of a classical subject, the individuals actually responsible for this achievement are the researchers who have developed this field. Carnot, who gave us an image of how heat works in engines, a view which I have taken as the starting point of my exposition. Gibbs demonstrated how to deal with chemical change and heat. Planck's theory of heat radiation still is one of the clearest expositions of the thermodynamics of radiation. Also, there are the researchers who have built continuum thermodynamics, mainly since the 1960s and who have contributed so much toward clarifying the foundations of the dynamics of heat. They deserve our respect for one of the most fascinating intellectual endeavors.

When it comes to applications we nowadays can turn to computational tools which can make life so much easier. Two such tools which I have used deserve to be mentioned—the system dynamics program Stella (High Performance Systems, Inc., Hanover, New Hampshire), and the program EES (Engineering Equation Solver; Klein, 1991) which provides for extensive thermophysical functions in addition to a solver for nonlinear equations and initial value problems. Also, in the fields of engineering applications, including solar engineering, I have been inspired by such excellent textbooks as those of Bejan (1988), Moran and Shapiro (1992), Rabl (1985), and Duffie and Beckman (1991).

I am grateful to all my friends, colleagues, and teachers who, through their encouragement and support, have contributed toward the writing of this book. Robert Resnick and Roland Lichtenstein of RPI gave me the courage to take up the project. Walter Cohen, Werner Maurer, and Martin Simon read the book and gave me valuable feedback. Heinz Juzi, Heinz Winzeler, and Klaus Wüthrich helped me with discussions of applications, and many more colleagues gave me kind words of encouragement. Most important, however, has been Werner Maurer's friendship and professional companionship in this endeavor. He and I developed the system dynamics approach to the teaching of physics which you will find in this book.

I would like to acknowledge generous grants made available by the Federal Government of Switzerland and my school, which allowed for the development of labs and courses dealing with renewable energy sources, and I would like to thank my thesis students whose work in solar energy engineering has led to many interesting applications included here.

Finally, let me express my gratitude toward all those at Springer-Verlag, who have made the production of the book possible. Thomas von Foerster, Frank Ganz, and Margaret Marynowski turned the manuscript of an amateur madly hacking away on a Macintosh into a professional product. They were very supportive and encouraging, always with an open mind for my wishes.

This has been a long journey. My wife and my daughter have gone through it with me all the way. I would like to thank them for their love and their patience. When my daughter was very little, she asked me if I would dedicate this book to her. I hope it has been worth waiting for.

Honolulu, 1995 *Hans Fuchs*

Table of Contents

PROLOGUE

A Unified View of Physical Processes

πavτα ρει

Heraclides (550-480)

Everything flows. Water and air flow on the surface of the Earth, where they create the multitude of phenomena we know from everyday life. Winds can impart their motion to the water of the oceans, and in a far-away place, this motion can be picked up again through the action of the waves. These processes are maintained by the radiation pouring out from the surface of the sun; light flows from there through space, and some of it is intercepted and absorbed by our planet. Both in nature and in machines, heat is produced and transported from place to place. In electrical machines, we make electricity flow in an imitation of its flow in the atmosphere, and in reactors, chemical substances flow while at the same time undergoing change. Today, we even see life as governed by flow processes.

We shall take this observation as the starting point of our investigation of natural and manmade phenomena. It leads to one of the most general description of nature we know today. There are a few physical quantities which can flow into and out of systems, which can be absorbed and emitted, and which can be produced and destroyed. Electrical charge is transported in electrical processes, and mass and substance flow in gravitational and chemical phenomena, respectively. In continuum mechanics, motion is seen as the exchange of linear and angular momentum. Thermal physics is the science of the transport and the production of heat. One of the great advantages of this description of nature is that it relates the different phenomena, which leads to an economical and unified view of physical processes. It turns out that classical continuum physics is a precise method of expressing this point of view for macroscopic systems (see Section P.5).

In this chapter, we shall present some examples of introductory physics, most of which you should be familiar with. We shall use as the main tool the images and the language found in continuum physics. In this way, we hope to prepare the ground for the approach to thermodynamics which you will find in this book. Note, however, that this chapter is a condensed overview, not a text. After reading Section P.1 you may want to venture directly into the main body of the book, in which case you might wish to return to this chapter later on. Either way, we believe you will find it advantageous to draw comparisons between different fields of physics as often as possible during your journey through thermodynamics.

What is this unified approach to physics? In short, it is based on an analogy with continuum physics. First, we have to agree on which physical quantities we are going to use as the fundamental or *primitive* ones; on their basis other quantities are defined, and laws are expressed with their help. Second, there are the fundamental *laws of balance* of the quantities which are exchanged in processes, such as momentum, charge, or amount of substance; we call these quantities *substancelike*. Third, we need particular laws governing the behavior of, or distinguishing between, different bodies; these laws are called *constitutive relations*. Last but not least, we need a means of relating different types of physical phenomena. The tool which permits us to do this is energy. We use the *energy principle*, i.e., the law which expresses our belief that there is a conserved quantity which appears in all phenomena, and which has a particular relationship with each of the types of processes.

To introduce the elements of theories listed above, we shall begin with a comparison of the flow of water and of electrical charge.

P.1 The Flow of Water and Charge

We all are familiar with the flow of water in simple settings, such as the filling or the discharging of containers through pipes (Figure 1). By looking at a special example we will be able to identify the elements of a physical theory which allow us to calculate such things as the current of water through a pipe, the pressure at various points in the fluid, and the time required to discharge a container. The analysis also will tell us that the system and the processes it may undergo are very similar to what we know from electricity. By comparing hydraulic and electrical systems we shall learn about the power of analogies between different fields of physics.

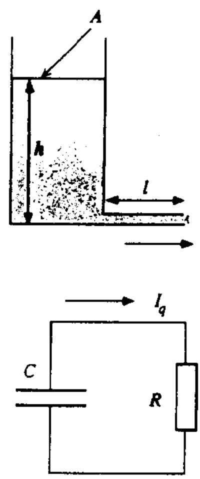

FIGURE 1. A simple container is filled with water up to a certain level. It can be discharged through a long thin pipe fitted at the bottom. This system and the processes it undergoes are comparable to a simple electrical circuit in which a capacitor is discharged through a resistor.

P.1.1 Physical Quantities

Our first question must be which physical quantities we can use as basis for a quantitative description of the flow of water into and out of containers. We shall have to do the same for the electrical system. The choice of fundamental or primitive quantities is not unique. We simply have to begin somewhere, in some way.

We certainly need a measure of the amount of water in a container. There are several possible choices. The simplest of these is the *volume* of the water. Another that comes to mind quickly is the *mass* of the water. Finally, chemists might be inclined to measure the amount of water on the basis of its *amount of substance* (Section P.2.7).

The last of the three measures is the most natural in the case envisioned. If we ask how much "stuff" is in a container, the amount of substance is preferable over the others. Mass (gravitational mass) is the measure of the property of bodies which gives rise to their weight. The volume, on the other hand, is a geometric measure. Therefore we ought to choose the amount of substance as our first primitive quantity. However, as long as there are no chemical reactions there is a simple and direct relationship between a body's amount of substance and its mass that allows us to choose the latter quantity instead of the former (Section P.2.7). Also, if we assume water to be incompressible, we can as well employ its volume as the measure we have been seeking. For this reason we shall express most of what follows in terms of the volume of a body of water. Still, it is important to be aware of the difference between the three quantities introduced so far. Volume is used as a convenient substitute for a body's amount of substance.

The case of electricity is very similar. The physical quantity which measures an amount of electricity is well known: it is the *electrical charge.* A capacitor stores a certain amount of charge, just as a container stores a certain volume of water.

Amount of substance and volume, as well as gravitational mass and electrical charge, are quantities which have a particular property in common. They scale with the system they describe. If a homogeneous body is divided into two equal pieces, each part "contains" half of the original quantity. For this reason these quantities are said to be *extensive.*

If we want to set up a theory of the flow of water we need a primitive quantity which describes its transport. For this purpose we conceive of the rate of flow of water, measured in terms of a new quantity which we call the *flux* of water. This quantity is measured, for example, at the outlet of the pipe shown in Figure 1. The rate at which water flows can be expressed in terms of the *volume flux* or *current of volume*, i.e., the volume of water flowing past a measuring device per time. Alternatively, we may employ the flux of mass or the flux of amount of substance. Again, for practical purposes, we shall choose the first of these measures for most of the following development. In electricity, the quantity analogous to volume flux is the *current of charge.*

Using volume and volume flux we are able to say something about an amount of water, namely the amount of water stored in a system, and the rate at which water is flowing. These quantities, however, do not suffice for a complete theory of the phenomena associated with containers of water and currents flowing in and out. They do not tell us anything about why water should be flowing at all. In electrical circuits as well, we need a quantity which is responsible for setting up currents of charge in the first place.

In addition to quantities measuring amounts of water, we need the *pressure* of the water to explain its flow through pipes. If the same rate of flow is to be sustained through two pipes of different diameters, the pressure difference between the inlets and the outlets of the pipes must be different. Different voltages, i.e. different differences of *electrical potential,* are required if the same electrical current is to pass through two different resistors. These examples demonstrate the nature of pressure and of electrical potential: they are quantities measuring an intensity rather than an amount of something. For this reason they are called *intensive* quantities. In contrast to the extensive quantities, intensive ones do not scale with the size of the system. If a body is divided into two parts, the intensive quantities are the same in both. Summing up, we may say:

To quantify physical phenomena we have to introduce measures of amounts and of intensities.

There is a very useful image which may be associated with intensive physical quantities. Since a difference of pressure or of electrical potential is necessary for water or charge to flow we may call such a difference a *driving force* for the process. In the flow of water on the surface of the Earth, a difference of levels commonly is the origin of the transport phenomena. Water falls from higher to lower levels by itself (Figure 2). The comparison of the flow of water or charge with waterfalls suggests that an intensive quantity may be imagined to be a *level*. Pressure therefore takes the role of the hydraulic level, while the electrical potential is visualized as the electrical level.

Note that hydraulics and electricity demonstrate a high degree of similarity — at least in the basic quantities employed. Naturally, only hindsight can tell us if we have chosen the right quantities as the fundamental ones for a given range of phenomena. This means that we have to accept a certain choice, define new quantities on its basis, build a theory, and work out its consequences. If we are satisfied with the results compared to what nature is demonstrating to us, we call the theory a successful one.

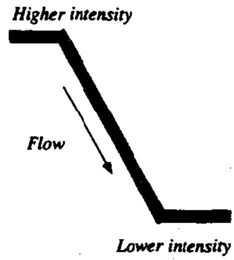

FIGURE 2. Both water in pipes and electrical charge in electrical circuits may be imagined to flow (by themselves) from regions of higher intensities of the potential associated with the phenomenon to regions of lower intensities. Graphically speaking, they flow from regions at high levels to regions at lower levels. This type of diagram is called a waterfall representation of physical processes.

P.1.2 Accounting

We want to know how much water is in a container at a given time. Alternatively, we want to say something about how the amount of water can change. For this purpose we shall conceive of a number of quantities which we will define on the basis of the fundamental ones introduced above. The first of these derived variables is the rate of change of the amount of water. Mathematics tells us how to define such a quantity. If we measure the amount of water in a container by its volume V, the rate of change of the volume is the time derivative dV/dt.

There is a simple but fundamental law which allows us to account for amounts of water. If the volume of water is a conserved quantity (as should be the case for incompressible fluids) the volume stored in a given system can change only due to the transport of water across the surface of the system (Figure 3). There must be currents or fluxes of volume with respect to the system, and they alone are responsible for the change of the contents of the system. This case is so simple that we can state right away the following law of balance of volume:

The rate of change of the volume of water in the system must be equal to the sum of all fluxes associated with the currents of water crossing the surface.

If we count the fluxes associated with currents leaving a system as positive quantities the law can be stated formally as follows:

$$\frac{dV}{dt} = -I_{V,net} \tag{1}$$

We shall use the symbol I for fluxes. Since there will be many fluxes for different physical phenomena, indices will be used to distinguish between them. Here, the index V stands for volume. The net flux simply is the sum of all fluxes occurring with respect to a system. Note that the quantity we call *flux* has the dimensions of the quantity which is flowing divided by time. (Often you will find in the literature the term *flux* associated with what we will call *flux density*, namely the rate of flow divided by the surface area through which the current is flowing. Here, we follow the tradition of electromagnetism, where we speak of electric or magnetic fluxes as the surface integrals of the flux densities, which are the quantities **E** or **B**.)

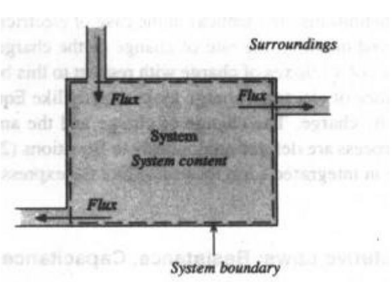

FIGURE 3. A system is a region of space occupied by a physical object. It is separated from the surroundings by its surface. Any physical quantity which we imagine to be stored in the system can change as a consequence of transport across its boundary. The transport is described in terms of currents, and fluxes measure the strength of the currents. Currents leaving a system are given positive fluxes. In some cases transport across the surface may be the only means of changing the contents.

Equation (1) is a fundamental law, namely the formal expression of our assumption that the volume of water is a conserved quantity. It is not a definition of the currents or fluxes of volume. The quantities occurring in Equation (1) are fundamentally different, related only by an interesting property of water. This property serves as one of the basic laws upon which we are going to build the following theory.

If we could no longer assume the volume of water to be a conserved quantity we would have to change the law of balance. We would be forced to account for other means of changing the volume, by introducing other terms in Equation (1). For now, let us assume that this is not necessary.

Often we are interested in the overall change of the volume of water in a container as the result of a process, not just in the rate of change. For this purpose we define two more physical quantities. The first is the *change of volume*, which is simply given by the integral over time of the rate of change of volume:

$$\Delta V = \int_{t_1}^{t_2} \dot{V} dt \tag{2}$$

The second quantity is the measure of how much water has flowed across the surface of the system in a given time. We shall call this quantity the *volume exchanged* in a process. It is defined as the (negative) integral over time of the fluxes of volume:

$$V_{e,net} = -\int_{t_1}^{t_2} I_{V,net} dt \qquad (3)$$

These two quantities allow us to express the law of balance of volume given in Equation (1) in the following form:

$$\Delta V = V_{e,net} \qquad (4)$$

Equation (4) again is a law of nature, while Equations (2) and (3) represent definitions. The law of balance expresses the simple fact that if volume is conserved, a change in the volume of fluid must be equal to the total volume which has crossed the surface of the system.

The laws and definitions are identical in the case of electricity. Since charge is a strictly conserved quantity, the rate of change of the charge of a body must be equal to the sum of all fluxes of charge with respect to this body. In other words, the law of balance of electrical charge looks exactly like Equation (1), with volume replaced by charge. The change of charge and the amount of charge exchanged in a process are defined analogously to Equations (2) and (3). Again, the law of balance in integrated form looks just like the expression in Equation (4).

P.1.3 Constitutive Laws: Resistance, Capacitance, and Inductance

The fundamental law of balance of the quantity we have chosen to represent the amount of water is not of much use by itself. Inspect it, and you will see that we can compute the rate of change of the volume of water in a container only if we have independent information regarding the fluxes. For this reason, a second class of fundamental laws—needed in a physical theory—are laws determining currents in given situations. Clearly such laws depend upon the particular circumstances. Therefore they are called *material laws* or *constitutive laws*.

In our example this means that we will have to state a law governing the flux of water through the particular pipe attached to the container (Figure 1). While Equation (1) is valid as long as the volume of water is a conserved quantity, the law for the flow of water through a pipe depends on many special material properties, and on special circumstances. The same is true for electrical currents as well.

Let us just state an example of a law for currents of water through pipes. Experience tells us that usually we have to force water through a pipe. In other words, there exists a *resistance* to the flow, and we need a driving force to maintain a current. If the fluid is considered to be viscous, and if the flow is laminar, the volume flux through a pipe is governed by the law of Hagen and Poiseuille:

$$I_V = -\frac{\pi r^4}{8\mu l}\Delta P \tag{5}$$

The flux depends linearly upon the difference between the pressures at the inlet and the outlet of the pipe. The factor multiplying the pressure difference depends upon the length l and the radius r of the pipe, and upon the viscosity μ of water. By the way, Equation (5) very much resembles Ohm's law in electricity. This type of relation is found for a number of dissipative constitutive laws, including diffusion and the conduction of heat.[1]

The inverse of the factor multiplying the potential difference is called the *(hydraulic) resistance*:

$$R_V = \frac{8\mu l}{\pi r^4} \tag{6}$$

In terms of this definition Hagen and Poiseuille's law may be expressed in the following simple and intuitive form:

$$I_V = -\frac{\Delta P}{R_V} \tag{7}$$

Constitutive laws specifying currents have to do with transport phenomena. Obviously, we also need a means of saying something about the process of storing water (or electrical charge). It is customary to introduce a quantity which expresses the relationship between a change of the amount of water contained in a system and the change of the associated potential, i.e., the change of pressure. This quantity is constitutive as well, since it depends on the type of system containing the water. It allows us to relate the change of system content to the possibly more easily measured potential. In electricity we are interested in the relationship between the charge contained in a system and the voltage.

Let us now turn to the constitutive quantity used to describe the storage of water in containers. The amount of water depends on the surface level h and the size of the container. For this reason we define the *capacitance* of the storage system: the capacitance is a quantity which indirectly determines the volume of water in the container. To be precise it is the quantity which tells us by how much the content increases if we increase the intensive quantity by one unit. In other words, the capacitance of a container shall be defined as

$$K = \frac{dV}{dP} \tag{8}$$

1. For a derivation of the law of Hagen and Poiseuille, and for a comparison of conductive transports of momentum, heat, and mass, see Bird, Stewart, and Lightfoot (1960) or any other book on transport phenomena.