The play of thermodynamics

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Part of a book on Thermodynamics
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This chapter outlines the play of thermodynamics, mostly written for teachers and for people who have studied thermodynamics.

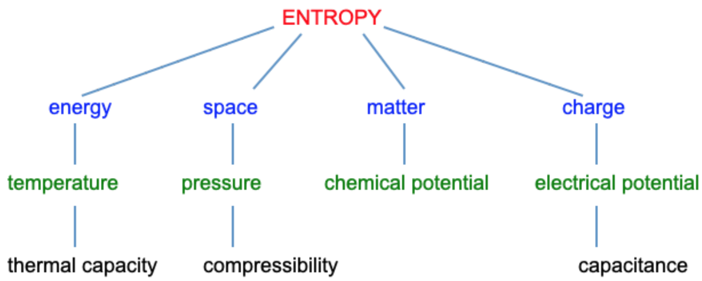
In class, I do not cover this chapter in one go. I pick a bit at a time, throughout the semester.

If at any point the reading gets hard, just skip ahead. Unlike watching a play, reading a script can be nonlinear. Return to this chapter for perspective.

Cast

I start the class by introducing the cast.

Entropy plays the leading role in thermodynamics. Thermodynamics is often called the science of energy. This designation steals accomplishments from other sciences, and diminishes accomplishments of thermodynamics. Rather, thermodynamics is the science of *entropy*.



What is entropy? Asking this question so early in the play is like asking, before the movie *The Godfather* starts, “Who is Michael Corleone?” You only get to know entropy after you watch the play of thermodynamics for some time. If you cannot wait, jump to the chapter on entropy.

Twitter What is X? (X = entropy, energy, temperature, pressure)
YouTube Popular science video on entropy

The Cast of Thermodynamics

Leading role:
Entropy

Supporting roles:
Energy
Space
Matter
Charge

Children of entropy and the supporting roles:
Temperature
Pressure
Chemical potential
Electrical potential

Grandchildren:
Thermal capacity
Compressibility
Coefficient of thermal expansion
Joule-Thomson coefficient
……

Shadows of entropy:
Massieu function
Planck function
Helmholtz function
Gibbs function
Exergy
……

Energy, space, matter, and charge are supporting roles of equal importance. In thermodynamics, energy plays a supporting role, along with space, matter, and charge. These supporting roles are analogous, of equal importance.

We are familiar with energy in various forms, such as the potential energy of a weight at a height, kinetic energy of a mass at a velocity, chemical energy in food and fuel, and electrical energy from transmission lines.

We are familiar with space in various aspects: length, area, and volume. A weight is raised in height. A fluid pushes a piston of a certain area, and expands in volume. In dispersion of ink, the volume confine pigment particles. A bottle confines molecules.

We are familiar with matter in various aggregates of molecules. In a half bottle of water, for example, H_2O molecules separate into two phases—water and steam.

We are also familiar with charge in terms of electrons and protons, as well as current and voltage.

This book does not have a chapter on space, matter, or charge, but does have a chapter on energy.

Children and grandchildren. Each of the supporting roles, together with entropy, produces a child. The four children—temperature, pressure, chemical potential, and electrical potential—are supporting roles of the second generation. They produce grandchildren: thermal capacity, compressibility, coefficient of thermal expansion, Joule-Thomson coefficient, etc.

Shadows of entropy. Entropy casts many shadows: Massieu function, Planck function, Helmholtz function, Gibbs function, exergy, etc. Let no shadows divert our attention from the thing itself—entropy.

Isolated system conserves energy, space, matter, and charge

We have met the cast. Now look at the stage—the *world*. A part of the world is called a *system*. The rest of the world is called the *surroundings*.

Our play begins with an *isolated system*—a part of the world that does not interact with the rest of the world.

Let us look at the four supporting actors: energy, space, matter, and charge. I make a half bottle of water into an isolated system. I close the bottle so that molecules can neither enter nor leave the bottle. I insulate the bottle to stop any energy transfer by vibration of atoms and radiation of light. I do not squeeze the bottle, so that the volume of the bottle is fixed. There is also no transfer of charge between the system and its surroundings.

Here are the *principles of conservation*:

An isolated system conserves energy, space, matter, and charge.

Exercise. Energy is liberated when hydrogen and oxygen explode. Does this observation violate the principle of the conservation of energy?

Exercise. Energy is liberated when water freezes. Does this observation violate the principle of the conservation of energy?

Exercise. Can you cool a kitchen by opening the door of a refrigerator?

Exercise. What are space, matter, and charge? Do you know why each is conserved?

Exercise. Baby Lucas has discovered a fact: the number of people that enter a room equals the change in the number of people in the room plus the number of people that leave the room. Explain this fact to baby Lucas. Will the phrase "the principle of the conservation of the number of people" be useful in your explanation?

Classification of systems

Depending on whether systems and their surroundings exchange matter, space, and energy, we classify systems into several types. For the time being, we neglect the transfer of charge.

	transfer matter	transfer space	transfer energy
isolated system	no	no	no
thermal system	no	no	yes
closed system	no	yes	yes
open system	yes	yes	yes

In this classification, a system is classified not by the content of the system, but by the interaction between the system and the surroundings. The classification drives the narrative of the play of thermodynamics.

Isolated system. By an *isolated system* we mean a part of the world that does not interact with the rest of the world.

When confused, isolate.

Isolated systems let entropy meet internal variables to define the basic algorithm of thermodynamics.

Thermal system. By a *thermal system* we mean a part of the world that interacts with the rest of the world in one mode: transfer energy by microscopic interaction, which is called *thermal contact*.

The word *thermal* is an adjective associated with microscopic interaction.

A half bottle of water is a thermal system. We cap the bottle to prevent molecules from leaking. We make the bottle rigid to fix its volume. We can still change the energy of the water by placing the bottle over a fire, by placing the bottle in a microwave oven, by shaking the bottle, or by passing an electric current through a resistor.

In the last case, the resistor is submerged in water. In the resistor, when electrons flow and bump atoms, the atoms do not change neighbors but vibrate. The vibration of the atoms of the resistor passes energy to water molecules. The sequence of events transfers energy from the electric current to water.

Thermal systems let entropy meet energy to define temperature.

Closed system. By a *closed system* we mean a part of the world that interacts with the rest of the world by transferring energy and space, but not matter.

Consider a gas in a cylinder, sealed by a piston, so that molecules will not leak. The gas in the cylinder interacts with the rest of the world in two ways. First, when weights are added over the piston, the piston moves down and reduces the volume of the gas. Second, when the cylinder is brought over a fire, the fire transfers energy to the gas by microscopic interaction.

Closed systems let entropy meet volume to define pressure.

Open system. By an *open system* we mean a part of the world that interacts with the rest of the world by transferring matter, space, and energy.

A bottle of wine, cap removed, is an open system. We smell the wine because molecules jump out of the wine. We can warm up the wine over a fire. We can change the volume of the wine by drinking it, or compressing it.

Open systems let entropy meet the number of molecules in a species to define chemical potential.

Exercise. Describe a method to keep water hot for a long time. What can you do to prolong the time? What makes water eventually cool down?

Exercise. For each type of system listed above, give an example. In each example, describe all modes of interaction between the system and its surroundings.

Beginners study these chapters first

Methods of thermodynamics are developed in the following chapters:

[Thermal system](#)
[Closed system](#)
[Open system](#)

Beginners studying on their own should begin with these chapters, with no digression. After these chapters, other chapters can be read in any order.

Intuition, logic, algorithm, data, application

This book will develop *intuition* of entropy from everyday experience, *logic* of entropy from the fundamental postulate, *algorithm* of entropy to direct calculation and measurement, *data* of entropy of various substances, and *application* of entropy in many disciplines.

The same intuition, logic, and algorithm, and data can be taught to everyone, but application is specific to each discipline. The situation is analogous to calculus. The same rules of differentiation and integration are taught to everyone, but application will be different for the engineer, economist, physiatrist, and chemist. Like calculus, thermodynamics belongs to many disciplines.

After the intuition, logic, algorithm, and data are in place, the engine will come as an application. You can choose to study it or not. The book contains many other applications, and will have more when I have time to learn and write, so that the book will help the reader master thermodynamics in any discipline. Multidisciplinary study is effective if we are disciplined.

Intuition

A logical place to start the play is the logic of thermodynamics. However, this logical starting point is removed from everyday experience.

Thermodynamics is an abstract subject, but has numerous concrete examples. We will begin with five:

Gas
Ice and water
Water and steam
Ice, water, and steam
Moist air

We will use these examples to sharpen our intuition. These examples at most mention entropy in passing. Later, after entropy is developed, we will return to these examples and relate them to entropy.

Twitter. Introductory examples of thermodynamics

Logic

The logic of thermodynamics requires some ideas in quantum mechanics and probability. But to see the logic of thermodynamics, you do not need to take a course on quantum mechanics or a course on probability. A few facts suffice. The logic of thermodynamics is formulated in the chapter on Isolated system, and is outlined here.

A. An isolated system flips among its quantum states. This fact of nature prompts us to use words in probability. An isolated system is an *experiment*. Each quantum state of the isolated system is an outcome of the experiment, called a *sample point*. All the quantum states of the isolated system constitute a set, called the *sample space*.
B. A system isolated for a long time flips to every one of its quantum states with equal probability. This fact of nature is called the *fundamental postulate*. Thus, isolating a system for a long time is analogous to rolling a fair die many times. A system isolated for a long time is said to be in *equilibrium*. Denote the number of quantum states of an isolated system by Ω. The system isolated for a long time flips to each of its quantum states with the same probability, 1/Ω.
C. A map from the sample space to another set is called a random variable in probability, and an *internal variable* in thermodynamics. For example, make a half bottle of water an isolated system. In the bottle, some H_2O molecules form water, and other H_2O molecules form steam. The number of H_2O molecules in steam is an internal variable.
D. When a constraint internal to an isolated system fixes an internal variable at a value x, the isolated system flips among the quantum states in a *subset* of the sample space. The number of quantum states in the subset is a function of the internal variable, Ω(x).
E. A subset of the sample space is called an event in probability, and is called a *state of constrained equilibrium* in thermodynamics. A system isolated for a long time, with an internal variable fixed at a value x for a long time, flips to every quantum state in the subset with equal probability, and is said to reach the state of constrained equilibrium at x.
F. Now lift the constraint and let the internal variable x vary for a long time. The probability for the internal variable to take value x is Ω(x)/Ω. The isolated system flips to a subset more likely if the subset has more quantum states.
G. Thermodynamics chooses an internal variable x such that the function Ω(x) peaks sharply. The peak of the function locates the average of x. The standard deviation of x is small compared to the average of x. Thermodynamics is devoted to the average of the internal variable.
H. When an internal variable changes from one value x = a to another value x = b, an isolated system is said to undergo a *process*. The beginning and the end of a process are specified by two states of constrained equilibrium, but the change between the beginning and end is in general not associated with any state of constrained equilibrium.

In the above, the word *state* is used in two senses: a “quantum state” and a “state of constrained equilibrium.” An isolated system has a sample space of quantum states. A subset of the sample space is called a state of constrained equilibrium.

Twitter The logic of thermodynamics

Algorithm

This logic leads to the *basic algorithm of thermodynamics*:

1. Construct an isolated system with an internal variable x.
2. Count the number of quantum states in a subset of the sample space of the isolated system as a function of the internal variable, $\Omega(x)$.
3. After the system is isolated and the internal variable x is allowed to vary, both for a long time, the system equilibrates at a value of x that maximizes $\Omega(x)$.
4. Let x = a and x = b be two states of constrained equilibrium. A process from a to b is *impossible* if $\Omega(a) > \Omega(b)$, *reversible* if $\Omega(a) = \Omega(b)$, and *irreversible* if $\Omega(a) < \Omega(b)$. All actual processes from a to b are irreversible, and have the same degree of irreversibility, $\Omega(b)/\Omega(a)$.

When a phenomenon involves an isolated system with multiple internal variables, the algorithm runs just the same.

The algorithm mentions neither energy nor entropy. In applying the algorithm to a phenomenon, energy enters as an internal variable. Other internal variables include volume and the number of molecules of each species.

Entropy. How does entropy come in? Let Ω be the number of quantum states of an isolated system. Define the entropy of the isolated system by

$$S = \log \Omega$$

We will explain why we hide Ω behind a log. Logarithm eases algebra, but adds no physics. Watch out! It is comical how entropy steals the show from the number of quantum states.

Subset entropy. When a constraint internal to an isolated system fixes an internal variable at a value x, the isolated system flips among the quantum states in a subset of the sample space. The number of quantum states in the subset is a function of the internal variable, $\Omega(x)$.

Define the *subset entropy* by

$$S(x) = \log \Omega(x)$$

Logarithm is an increasing function. Increasing $\Omega(x)$ is equivalent to increasing $S(x)$. We can restate the basic algorithm of thermodynamics in terms of subset entropy $S(x)$.

Twitter Basic algorithm of thermodynamics

Define second-generation supporting roles: temperature, pressure, and chemical potential. We have met an all-star cast of actors. Let us watch them play, act by act. Thermodynamics uses conserved quantities—energy, space, matter—as internal variables. Of course, internal variables need not be restricted to conserved quantities. This said, all conserved quantities obey similar arithmetics, and are convenient to study in parallel:

- Act One: Thermal system defines temperature
- Act Two: Closed system defines pressure
- Act Three: Open system defines chemical potential

We analyze thermal systems, closed systems, and open systems by constructing isolated systems with internal variables, following the basic algorithm of thermodynamics.

Data

Step 2 of the basic algorithm of thermodynamics instructs us to *count* the number of quantum states in a subset of the sample space of the isolated system as a function of the internal variable, $\Omega(x)$.

How do we count?

In thermodynamics, the number of quantum states is counted by *experimental measurements*. The number of quantum states is also counted theoretically in statistical mechanics. This book is devoted to thermodynamics, not statistical mechanics.

Instead of asking what quantum states are, thermodynamics counts them–experimentally.

Ours is the Age of Molecules and the Age of Data. Molecules generate data. The basic algorithm of thermodynamics guides us to measure, curate, and use the data.

Thermodynamic data are measured in many disciplines, including materials science, thermal physics, thermochemistry, electrochemistry, and biochemistry.

This course will study many datasets:

- Pure substance
- Incompressible pure substance
- Ideal gas
- Ideal gas mixture
- Enthalpy of formation
- Absolute entropy

Steam tables list temperature, pressure, volume, energy, enthalpy, and entropy of a single species of molecules, H_2O, in various states. The development of the steam tables perhaps is the first example of "data-driven science". Similar tables exist for numerous other species of molecules, most notably for refrigerants.

For each species of molecules, ideal gas tables list enthalpy and entropy as functions of temperature. These tables are used to analyze mixing and reaction of any number of ideal gases.

Here is a compilation of data, which we will learn to use throughout the course.

Solids and liquids that mix many species of molecules generate enormous amounts of data. Gathering these data remains an unfinished business, and has become a part of the Material Genome Initiative. Innovations are anticipated in experimental methods and machine learning.

Twitter Steam Tables as a Big Data Project

Application

Every application of thermodynamics displays the same pattern as follows.

Describe a phenomenon. Examples include the function of a throttle, the ascent of sap, the cycle in a power plant, the molecules in a reaction, and the run of a fuel cell.

Run the basic algorithm of thermodynamics. Identify an isolated system with internal variables. Determine states of equilibrium and direction of process.

Use data. Examples of data include properties of pure substances, incompressible pure substances, ideal gases, and ideal gas mixtures.

Make predictions. Examples include conditions of chemical equilibrium, direction of a chemical reaction, and efficiency of an engine.

Textbooks contain copious examples of application. This book describes some:

- Phase transition
- Chemical reaction
- Carnot engine
- Steady flow devices
- Power and refrigeration
- Psychrometrics (Heating, ventilation, and air-conditioning)
- The ascent of sap in a tree
- Fuel cell
- Chemical equilibrium

All these applications, particularly the Carnot engine, historically contributed to the development of thermodynamics. All applications, however, are incidental to the logic of thermodynamics. You can master thermodynamics without studying the Carnot engine, but you do need to work through many applications.

Thermodynamics makes sense only if one empathizes with the experimentalist.

The situation is similar in calculus. The calculation of the orbits of planets historically contributed to the development of calculus, but is incidental to the logic of calculus. You can master calculus without studying the orbits of planets, but you do need to work through many applications.

Exercise. Find courses on thermodynamics and statistical mechanics on campus. Compare the contents of the courses.

Thermodynamics for everyone

Thermodynamics should be a play for everyone, just as English, physics, chemistry, and calculus should. The logic of thermodynamics is expressed mostly in English, with a little physics, chemistry, and calculus.

English is a wonderful language, but was not invented for thermodynamics. I will mostly use nouns and verbs, and mostly avoid adjectives. Along with words, I will use pictures, videos, and equations. A picture is worth a thousand words. A video is worth a thousand pictures. An equation is worth a thousand videos. By this reckoning, an equation is worth a billion words.

But that is an understatement. For example, in mechanics, the equation $f = ma$ generates countless words, pictures, and videos. In thermodynamics, the equation

$$dS(U)/dU = 1/T$$

links three quantities: entropy S, energy U, and temperature T. This equation illustrates the use of calculus. The equation says that temperature is a child—a derivative—of entropy and energy. It is quick to write such an equation, but takes time to relate the equation to words, pictures, and videos. It takes even more time to stitch them all—words, pictures, videos, and equations—into the fabric of nature.

But what are entropy and energy? They are facts of nature, distilled in physics and chemistry. A few facts of nature are more significant than others to the logic of thermodynamics. I will try to make these facts familiar to you, and will not hide them from you.

A girl meets a boy. They fall in love. They live happily ever after. How many times have we heard this story? Yet we keep telling it. Each telling is as fresh as that by Homer or

Shakespeare. It is a great story, has endless variations, and is fundamental to many other stories. It is a story to experience for many lifetimes.

So is thermodynamics. After this play, you will recognize a story of thermodynamics no matter how it is told. Aha, you will say, this is yet another play of thermodynamics! One day, you will tell your own story of thermodynamics. You cannot avoid telling the story so long as you stay in touch with nature. Thermodynamics is a fundamental play of nature.

The great play of thermodynamics has not found a worthy writer like Homer or Shakespeare. Be that worthy writer, or make do with a writer like this one.

Thermodynamics can be a subject of “Liberal Arts Education”—a curriculum to gain ability to think critically and learn any subject, instead of skills for a profession.

Wikipedia Liberal Arts Education
Twitter Thermodynamics as a subject of Liberal Arts Education

History

Set wood on fire, the fire turns water into steam, and the steam raises a weight to a height. Humans have learned to set fire for over a million years, and have learned to use steam to push something for thousands of years. These skills prepared humans to launch the Industrial Revolution in the eighteenth century.

YouTube Hero’s engine
Wikipedia Aeolipile
Wikipedia Control of fire by early humans

At the height of the Industrial Revolution, Carnot (1824) asked, How does an amount of coal lift the heaviest weight to a height? In answering this question, he conceived the notion of entropy. Clausius (1854) related entropy to energy and temperature, and coined the word “entropy” in 1865. Boltzmann (1877) linked entropy to microstates of molecules. Planck (1900) discovered quantum states. Gibbs (1873, 1901) shaped the science of entropy into the form as we use today.

What did the word “thermodynamics” come from? Carnot (1824) titled his little book “Reflections on the Motive Power of Fire.” By “motive power” he meant “the useful effect that a motor is capable of producing. This effect can always be likened to the elevation of a weight to a certain height. It has, as we know, as a measure, the product of weight multiplied by the height to which it is raised.”

Kelvin (1854) coined the word “thermodynamics.” The nature of “thermo” (heat) was obscure then. Dynamics has its origin in the Greek word dynamis, "force, power."

We now know that "being thermal" is about microscopic interaction. Today, thermodynamics links the microscopic and the macroscopic.

1824 Carnot, Reflections on Motive Power of Fire. Tweet
1854 Kelvin On the dynamical theory of heat. Twitter

The science of entropy has grown far beyond Carnot's concern over burning coal to lift weights. Applications include engines, phases, mixtures, reactions, batteries, surfaces, and deformations. Opening books on physics, chemistry, biology, environmental science, materials science, and food science, you find long chapters on thermodynamics. Many disciplines in science and engineering require students to take a course on thermodynamics. The word "entropy" has entered popular culture. All publicity is good publicity, some scientists say. Others protest.

This book does not teach the history of thermodynamics. It is impractical to teach thermodynamics by tracing the steps (and missteps) of the creators, just as it is impractical to teach calculus by tracing the steps of Newton and Leibniz and quarrels between them. A subject and its history are different things. Mixing them in an introductory course does injustice to both. The path of discovery was tortuous, but the path of an introductory course is straight.

Tweeter. On the shoulder of a giant

Great steps inspire, great missteps teach. This said, the history of thermodynamics is illuminating and well-documented, full of dramas of triumph and despair. Nature works without science. But humans create science to understand nature. To study science is to study nature *and* humans. We celebrate past creators, and nurture future ones. We hold deep conversations with other humans in distant lands and times. We build a collective memory that helps humans survive, prosper, and be happy.

Missteps of creators leave scars in thermodynamics, some of which are unhealed to this day. Healing may expedite if we learn some history. Great steps inspire, great missteps teach.

I will place a few names and years in this book as landmarks. You can read the history of thermodynamics online, starting with this Wikipedia page.

History was not created by historians. Go dip into the works of creators. Even a cursory reading of an original paper enhances your enjoyment of the play, and lets you have a dialogue with a creator across time and land. Stars shine before street lamps pollute the sky.

Here are some of the landmark papers in the creation of thermodynamics.

Ignore the laws

To apply entropy to an engine, you need to know entropy *and* the engine. This historical development was hard in discovering entropy in the nineteenth century, and is even harder in learning entropy today. Students today rarely have first-hand knowledge of engines, and many will never care about engines. I forgo the historical development, and do not use any engine to develop the logic of entropy.

An average person knows many facts of nature. Energy transfers from a hot place to a cold place. Friction warms things. Ice melts in hands. Ink disperses in water. Perfume smells. Scientists know to conserve energy, but minimize free energy.

Yet, even many great scientists feel uncomfortable with the laws of thermodynamics. Let us hear the child and trust our own eyes—the emperor has no clothes. Feeling entropy through the second law is like blind people feeling an elephant. It is odd for teachers to hide what entropy is. Students are not blind, and should not be blindfolded.

Many books, including Reif (1965), Kittel-Kroemer (1980), Landau-Lifshtz (1980), Callen (1985), mention the laws of thermodynamics in passing.

I will not structure this play of thermodynamics around the zeroth, first, and second laws. It is often claimed that these laws define three properties: temperature, internal energy, and entropy. This claim is false. I will mention the laws in passing, so you see how they mislead:

- The zeroth law of thermodynamics
- The first law of thermodynamics
- The second law of thermodynamics

These laws have served historical purposes. They belong to museums, not to an introduction to the current practice. The situation is reminiscent of Chinese medicine. The medicine works, but the theory of medicine is faulty, made up before the facts of nature came to light.

In teaching thermodynamics, I ignore these laws out of respect for both the laws and students. Let these laws be admired in museums. Let students live in the world mostly and visit museums occasionally.

I will focus on the algorithm that directs calculation and measurement, in a way that thermodynamics has been practiced since the time of Gibbs (1873). You will learn to run the algorithm on everything thermodynamic.

Twitter These laws do injustice to both students and thermodynamics

Postulates and facts

I play down the laws of thermodynamics for another reason. Geometry must have impressed the creators of thermodynamics. In geometry, a few facts, labeled as postulates (i.e., laws), derive all other facts.

Thermodynamics has never been practiced this way. A few facts do play special roles in setting up the basic algorithm of thermodynamics, but are insufficient to derive most other facts. For example, we will use the algorithm to develop a theory of temperature and a theory of melting, but these theories do not predict this fact: ice melts at zero Celsius.

Postulational geometry is a wrong model for thermodynamics, and is even a wrong model for practical use of geometry. In thermodynamics, numerous facts are significant, and cannot be derived from other facts. You will have to learn numerous facts individually. Most facts do not fit in any simplistic scheme of postulates and derived facts.

Watch the Feynman Lecture on the relation between mathematics and physics. His discussion on Greek and Babylonian traditions of mathematics starts at 23:30.

New synthesis of thermodynamics

Fundamental postulate. After Planck (1900) discovered quantum states, a new synthesis of thermodynamics started on the basis of a fundamental postulate:

A system isolated for a long time flips to every one of its quantum states with equal probability.

For an isolated system consisting of many particles, this postulate of probability makes predictions of (almost) certainty. In particular, the fundamental postulate predicts the zeroth, second, and third laws.

This new synthesis is described in many textbooks, including Reif (1965), Kittel-Kroemer (1980), and Landau-Lifshetz (1980).

Algorithm, its formulation and application. This book is devoted to the new synthesis of thermodynamics. I divide the new synthesis into two parts. One part formulates the basic algorithm of thermodynamics, and the other part applies the algorithm to various situations. The algorithm focuses exclusively on entropy. The algorithm does not mention supporting actors, but provides a port for their entry. The supporting actors enter in the applications of the algorithm to various situations. For example, the union of entropy and energy produces temperature.

Incidentally, the fundamental postulate leads to two algorithms: the basic algorithm of thermodynamics, and the basic algorithm of statistical mechanics. The former is described in this book, and the latter is described elsewhere.