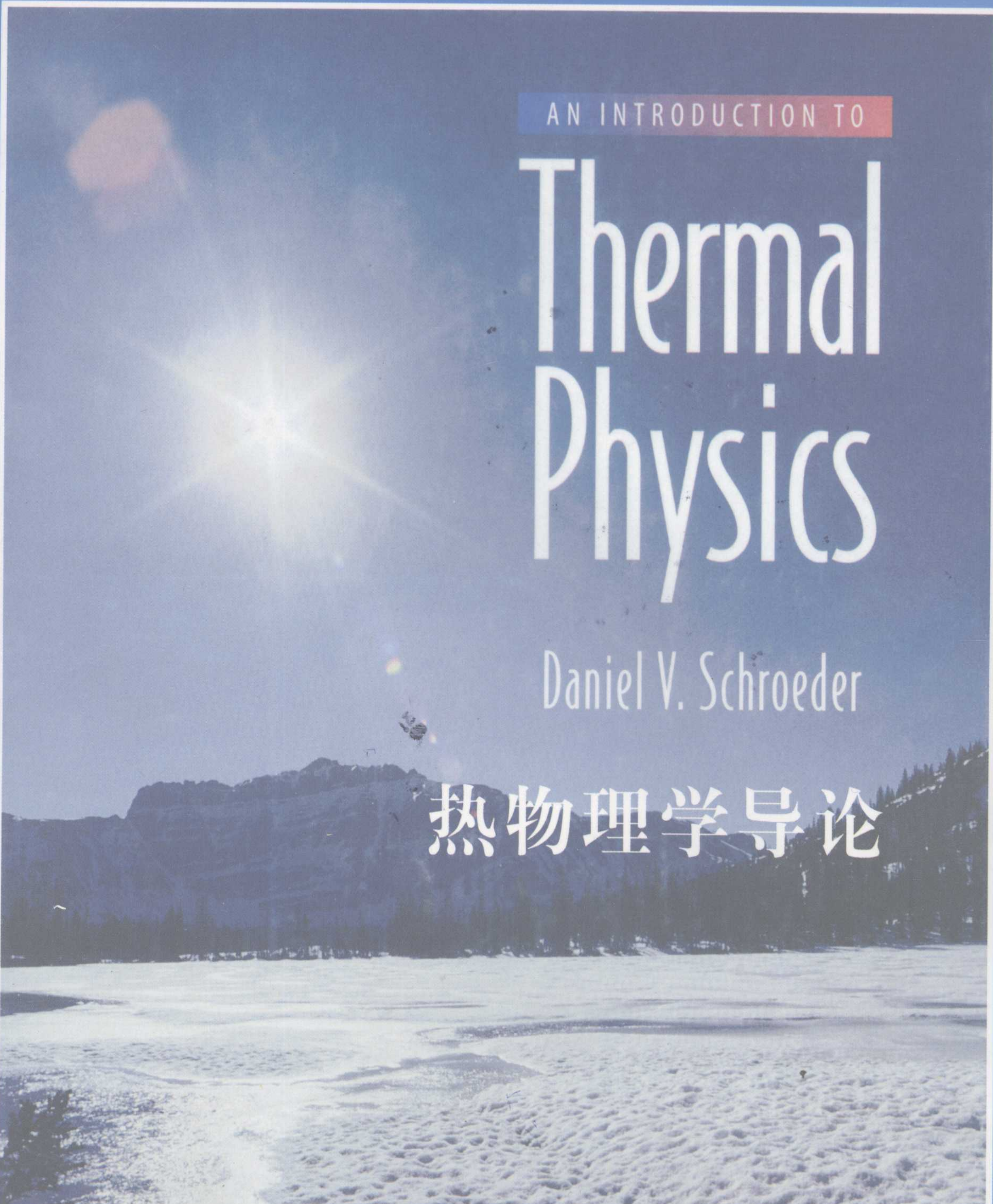

AN INTRODUCTION TO

Thermal Physics

Daniel V. Schroeder

热物理学导论

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AN INTRODUCTION TO

Thermal Physics

Daniel V. Schroeder

Weber State University

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Preface

Thermal physics deals with collections of *large* numbers of particles—typically 10^{23} or so. Examples include the air in a balloon, the water in a lake, the electrons in a chunk of metal, and the photons (electromagnetic wave packets) given off by the sun. Anything big enough to see with our eyes (or even with a conventional microscope) has enough particles in it to qualify as a subject of thermal physics.

Consider a chunk of metal, containing perhaps 10^{23} ions and 10^{23} conduction electrons. We can't possibly follow every detail of the motions of all these particles, nor would we want to if we could. So instead, in thermal physics, we assume that the particles just jostle about randomly, and we use the laws of probability to predict how the chunk of metal as a whole ought to behave. Alternatively, we can measure the bulk properties of the metal (stiffness, conductivity, heat capacity, magnetization, and so on), and from these infer something about the particles it is made of.

Some of the properties of bulk matter don't really depend on the microscopic details of atomic physics. Heat always flows spontaneously from a hot object to a cold one, never the other way. Liquids always boil more readily at lower pressure. The maximum possible efficiency of an engine, working over a given temperature range, is the same whether the engine uses steam or air or anything else as its working substance. These kinds of results, and the principles that generalize them, comprise a subject called **thermodynamics**.

But to understand matter in more detail, we must also take into account both the quantum behavior of atoms and the laws of statistics that make the connection between one atom and 10^{23}. Then we can not only *predict* the properties of metals and other materials, but also explain *why* the principles of thermodynamics are what they are—why heat flows from hot to cold, for example. This underlying explanation of thermodynamics, and the many applications that come along with it, comprise a subject called **statistical mechanics**.

Physics instructors and textbook authors are in bitter disagreement over the proper content of a first course in thermal physics. Some prefer to cover only thermodynamics, it being less mathematically demanding and more readily applied to the everyday world. Others put a strong emphasis on statistical mechanics, with

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its spectacularly detailed predictions and concrete foundation in atomic physics. To some extent the choice depends on what application areas one has in mind: Thermodynamics is often sufficient in engineering or earth science, while statistical mechanics is essential in solid state physics or astrophysics.

In this book I have tried to do justice to *both* thermodynamics and statistical mechanics, without giving undue emphasis to either. The book is in three parts. Part I introduces the fundamental principles of thermal physics (the so-called first and second laws) in a unified way, going back and forth between the microscopic (statistical) and macroscopic (thermodynamic) viewpoints. This portion of the book also applies these principles to a few simple thermodynamic systems, chosen for their illustrative character. Parts II and III then develop more sophisticated techniques to treat further applications of thermodynamics and statistical mechanics, respectively. My hope is that this organizational plan will accomodate a variety of teaching philosophies in the middle of the thermo-to-statmech continuum. Instructors who are entrenched at one or the other extreme should look for a different book.

The thrill of thermal physics comes from using it to understand the world we live in. Indeed, thermal physics has so *many* applications that no single author can possibly be an expert on all of them. In writing this book I've tried to learn and include as many applications as possible, to such diverse areas as chemistry, biology, geology, meteorology, environmental science, engineering, low-temperature physics, solid state physics, astrophysics, and cosmology. I'm sure there are many fascinating applications that I've missed. But in my mind, a book like this one cannot have too many applications. Undergraduate physics students can and do go on to specialize in all of the subjects just named, so I consider it my duty to make you aware of some of the possibilities. Even if you choose a career entirely outside of the sciences, an understanding of thermal physics will enrich the experiences of every day of your life.

One of my goals in writing this book was to keep it short enough for a one-semester course. I have failed. Too many topics have made their way into the text, and it is now too long even for a very fast-paced semester. The book is still intended primarily *for* a one-semester course, however. Just be sure to omit several sections so you'll have time to cover what you *do* cover in some depth. In my own course I've been omitting Sections 1.7, 4.3, 4.4, 5.4 through 5.6, and all of Chapter 8. Many other portions of Parts II and III make equally good candidates for omission, depending on the emphasis of the course. If you're lucky enough to have *more* than one semester, then you can cover all of the main text and/or work some extra problems.

Listening to recordings won't teach you to play piano (though it can help), and reading a textbook won't teach you physics (though it too can help). To encourage you to learn actively while using this book, the publisher has provided ample margins for your notes, questions, and objections. I urge you to read with a pencil (not a highlighter). Even more important are the problems. All physics textbook authors tell their readers to work the problems, and I hereby do the same. In this book you'll encounter problems every few pages, at the end of almost every section. I've put them there (rather than at the ends of the chapters) to get your attention, to show you at every opportunity what you're now capable of doing. The problems come in all types: thought questions, short numerical calculations, order-of-magnitude estimates, derivations, extensions of the theory, new applications, and extended projects. The time required per problem varies by more than three orders of magnitude. Please work as many problems as you can, early and often. You won't have time to work all of them, but please *read* them all anyway, so you'll know what you're missing. Years later, when the mood strikes you, go back and work some of the problems you skipped the first time around.

Before reading this book you should have taken a year-long introductory physics course and a year of calculus. If your introductory course did not include any thermal physics you should spend some extra time studying Chapter 1. If your introductory course did not include any quantum physics you'll want to refer to Appendix A as necessary while reading Chapters 2, 6, and 7. Multivariable calculus is introduced in stages as the book goes on; a course in this subject would be a helpful, but not absolutely necessary, corequisite.

Some readers will be disappointed that this book does not cover certain topics, and covers others only superficially. As a partial remedy I have provided an annotated list of suggested further readings at the back of the book. A number of references on particular topics are given in the text as well. Except when I have borrowed some data or an illustration, I have not included any references merely to give credit to the originators of an idea. I am utterly unqualified to determine who deserves credit in any case. The occasional historical comments in the text are grossly oversimplified, intended to tell how things *could* have happened, not necessarily how they did happen.

No textbook is ever truly finished as it goes to press, and this one is no exception. Fortunately, the World-Wide Web gives authors a chance to continually provide updates. For the foreseeable future, the web site for this book will be at `http://physics.weber.edu/thermal/`. There you will find a variety of further information including a list of errors and corrections, platform-specific hints on solving problems requiring a computer, and additional references and links. You'll also find my e-mail address, to which you are welcome to send questions, comments, and suggestions.

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It is a pleasure to thank the many people who have contributed to this project.

First there are the brilliant teachers who helped me learn thermal physics: Philip Wojak, Tom Moore, Bruce Thomas, and Michael Peskin. Tom and Michael have continued to teach me on a regular basis to this day, and I am sincerely grateful for these ongoing collaborations. In teaching thermal physics myself, I have especially depended on the insightful textbooks of Charles Kittel, Herbert Kroemer, and Keith Stowe.

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them, and to their students, for enduring the many inconveniences of an unfinished textbook. I owe special thanks to my own students from seven years of teaching thermal physics at Grinnell College and Weber State University. I'm tempted to list all their names here, but instead let me choose just three to represent them all: Shannon Corona, Dan Dolan, and Mike Shay, whose questions pushed me to develop new approaches to important parts of the material.

Others who generously took the time to read and comment on early drafts of the manuscript were Elise Albert, W. Ariyasinghe, Charles Ebner, Alexander Fetter, Harvey Gould, Ying-Cheng Lai, Tom Moore, Robert Pelcovits, Michael Peskin, Andrew Rutenberg, Daniel Styer, and Larry Tankersley. Farhang Amiri, Lee Badger, and Adolph Yonkee provided essential feedback on individual chapters, while Colin Inglefield, Daniel Pierce, Spencer Seager, and John Sohl provided expert assistance with specific technical issues. Karen Thurber drew the magician and rabbit for Figures 1.15, 5.1, and 5.9. I am grateful to all of these individuals, and to the dozens of others who have answered questions, pointed to references, and given permission to reproduce their work.

I thank the faculty, staff, and administration of Weber State University, for providing support in a multitude of forms, and especially for creating an environment in which textbook writing is valued and encouraged.

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1 Energy in Thermal Physics

1.1 Thermal Equilibrium

The most familiar concept in thermodynamics is **temperature**. It's also one of the trickiest concepts—I won't be ready to tell you what temperature *really* is until Chapter 3. For now, however, let's start with a very naive definition:

> **Temperature** is what you measure with a thermometer.

If you want to measure the temperature of a pot of soup, you stick a thermometer (such as a mercury thermometer) into the soup, wait a while, then look at the reading on the thermometer's scale. This definition of temperature is what's called an **operational definition**, because it tells you how to *measure* the quantity in question.

Ok, but why does this procedure work? Well, the mercury in the thermometer expands or contracts, as its temperature goes up or down. Eventually the temperature of the mercury equals the temperature of the soup, and the volume occupied by the mercury tells us what that temperature is.

Notice that our thermometer (and any other thermometer) relies on the following fundamental fact: When you put two objects in contact with each other, and wait long enough, they tend to come to the same temperature. This property is so fundamental that we can even take it as an alternative *definition* of temperature:

> **Temperature** is the thing that's the same for two objects, after they've been in contact long enough.

I'll refer to this as the **theoretical definition** of temperature. But this definition is extremely vague: What kind of "contact" are we talking about here? How long is "long enough"? How do we actually ascribe a numerical value to the temperature? And what if there is more than one quantity that ends up being the same for both objects?

Before answering these questions, let me introduce some more terminology:

> After two objects have been in contact long enough, we say that they are in **thermal equilibrium**.
>
> The time required for a system to come to thermal equilibrium is called the **relaxation time**.

So when you stick the mercury thermometer into the soup, you have to wait for the relaxation time before the mercury and the soup come to the same temperature (so you get a good reading). After that, the mercury is in thermal equilibrium with the soup.

Now then, what do I mean by "contact"? A good enough definition for now is that "contact," in this sense, requires some means for the two objects to exchange energy spontaneously, in the form that we call "heat." Intimate mechanical contact (i.e., touching) usually works fine, but even if the objects are separated by empty space, they can "radiate" energy to each other in the form of electromagnetic waves. If you want to *prevent* two objects from coming to thermal equilibrium, you need to put some kind of thermal insulation in between, like spun fiberglass or the double wall of a thermos bottle. And even then, they'll eventually come to equilibrium; all you're really doing is increasing the relaxation time.

The concept of relaxation time is usually clear enough in particular examples. When you pour cold cream into hot coffee, the relaxation time for the contents of the cup is only a few seconds. However, the relaxation time for the coffee to come to thermal equilibrium with the surrounding room is many minutes.*

The cream-and-coffee example brings up another issue: Here the two substances not only end up at the same temperature, they also end up blended with each other. The blending is not necessary for *thermal* equilibrium, but constitutes a second type of equilibrium—**diffusive equilibrium**—in which the molecules of each substance (cream molecules and coffee molecules, in this case) are free to move around but no longer have any tendency to move one way or another. There is also **mechanical equilibrium**, when large-scale motions (such as the expansion of a balloon—see Figure 1.1) can take place but no longer do. For each type of equilibrium between two systems, there is a quantity that can be exchanged between the systems:

Exchanged quantity	Type of equilibrium
energy	thermal
volume	mechanical
particles	diffusive

Notice that for thermal equilibrium I'm claiming that the exchanged quantity is *energy.* We'll see some evidence for this in the following section.

When two objects are able to exchange energy, and energy tends to move spontaneously from one to the other, we say that the object that gives up energy is at

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*Some authors define relaxation time more precisely as the time required for the temperature difference to decrease by a factor of $e \approx 2.7$. In this book all we'll need is a qualitative definition.

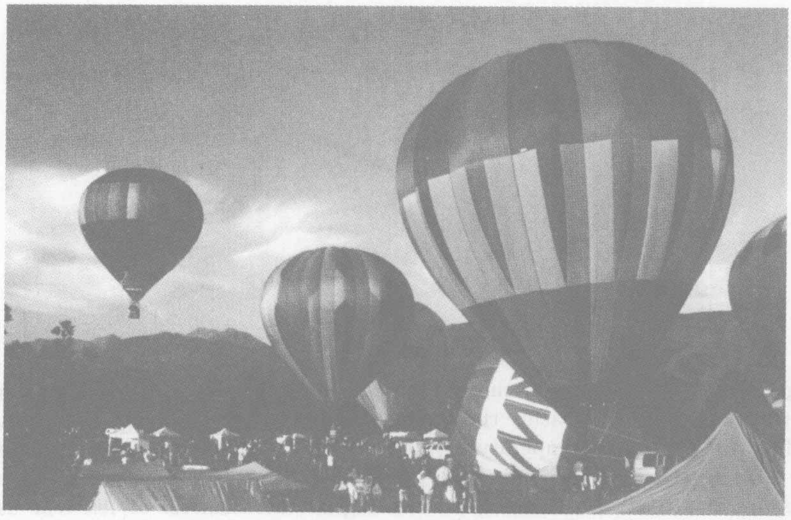

Figure 1.1. A hot-air balloon interacts thermally, mechanically, and diffusively with its environment—exchanging energy, volume, and particles. Not all of these interactions are at equilibrium, however.

a *higher* temperature, and the object that sucks in energy is at a *lower* temperature. With this convention in mind, let me now restate the theoretical definition of temperature:

> **Temperature** is a measure of the tendency of an object to spontaneously give up energy to its surroundings. When two objects are in thermal contact, the one that tends to spontaneously *lose* energy is at the *higher* temperature.

In Chapter 3 I'll return to this theoretical definition and make it much more precise, explaining, in the most fundamental terms, what temperature really *is*.

Meanwhile, I still need to make the *operational* definition of temperature (what you measure with a thermometer) more precise. How do you make a properly calibrated thermometer, to get a numerical *value* for temperature?

Most thermometers operate on the principle of thermal expansion: Materials tend to occupy more volume (at a given pressure) when they're hot. A mercury thermometer is just a convenient device for measuring the volume of a fixed amount of mercury. To define actual *units* for temperature, we pick two convenient temperatures, such as the freezing and boiling points of water, and assign them arbitrary numbers, such as 0 and 100. We then mark these two points on our mercury thermometer, measure off a hundred equally spaced intervals in between, and declare that this thermometer now measures temperature on the Celsius (or centigrade) scale, by definition!

Of course it doesn't have to be a mercury thermometer; we could instead exploit the thermal expansion of some other substance, such as a strip of metal, or a gas at fixed pressure. Or we could use an electrical property, such as the resistance, of some standard object. A few practical thermometers for various purposes are shown

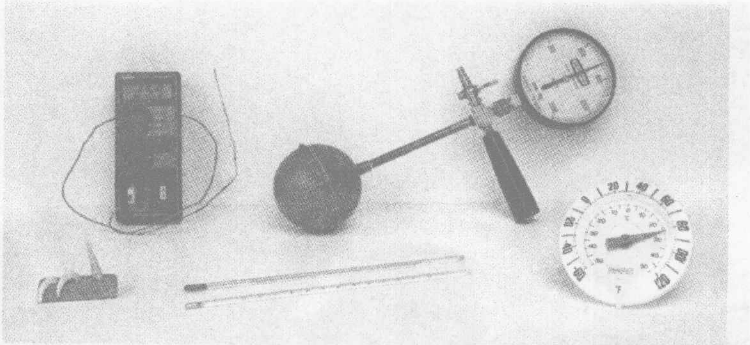

Figure 1.2. A selection of thermometers. In the center are two liquid-in-glass thermometers, which measure the expansion of mercury (for higher temperatures) and alcohol (for lower temperatures). The dial thermometer to the right measures the turning of a coil of metal, while the bulb apparatus behind it measures the pressure of a fixed volume of gas. The digital thermometer at left-rear uses a thermocouple—a junction of two metals—which generates a small temperature-dependent voltage. At left-front is a set of three potter's cones, which melt and droop at specified clay-firing temperatures.

in Figure 1.2. It's not obvious that the scales for various different thermometers would agree at all the intermediate temperatures between 0°C and 100°C. In fact, they generally won't, but in many cases the differences are quite small. If you ever have to measure temperatures with great precision you'll need to pay attention to these differences, but for our present purposes, there's no need to designate any one thermometer as the official standard.

A thermometer based on expansion of a gas is especially interesting, though, because if you extrapolate the scale down to very low temperatures, you are led to predict that for any low-density gas at constant pressure, the volume should go to *zero* at approximately −273°C. (In practice the gas will always liquefy first, but until then the trend is quite clear.) Alternatively, if you hold the volume of the gas fixed, then its *pressure* will approach zero as the temperature approaches −273°C (see Figure 1.3). This special temperature is called **absolute zero**, and defines the zero-point of the **absolute temperature scale**, first proposed by William Thomson in 1848. Thomson was later named Baron Kelvin of Largs, so the SI unit of absolute temperature is now called the **kelvin**.* A kelvin is the same size as a degree Celsius, but kelvin temperatures are measured up from absolute zero instead of from the freezing point of water. In round numbers, room temperature is approximately 300 K.

As we're about to see, many of the equations of thermodynamics are correct *only* when you measure temperature on the kelvin scale (or another absolute scale such as the Rankine scale defined in Problem 1.2). For this reason it's usually wise

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*The Unit Police have decreed that it is impermissible to say "degree kelvin"—the name is simply "kelvin"—and also that the names of all Official SI Units shall not be capitalized.

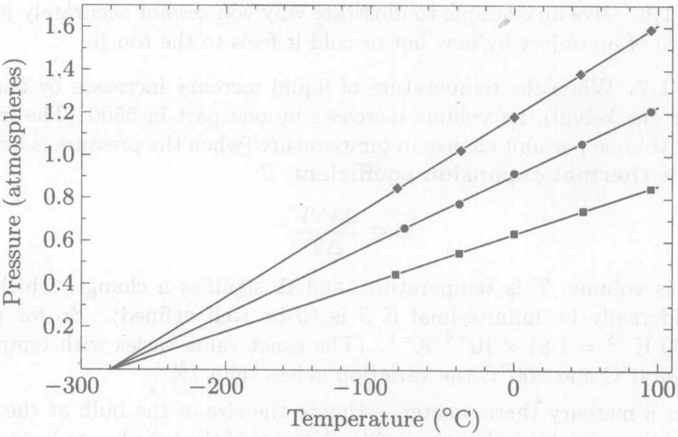

Figure 1.3. Data from a student experiment measuring the pressure of a fixed volume of gas at various temperatures (using the bulb apparatus shown in Figure 1.2). The three data sets are for three different amounts of gas (air) in the bulb. Regardless of the amount of gas, the pressure is a linear function of temperature that extrapolates to zero at approximately −280°C. (More precise measurements show that the zero-point does depend slightly on the amount of gas, but has a well-defined limit of −273.15°C as the density of the gas goes to zero.)

to convert temperatures to kelvins before plugging them into any formula. (Celsius is ok, though, when you're talking about the *difference* between two temperatures.)

Problem 1.1. The Fahrenheit temperature scale is defined so that ice melts at 32°F and water boils at 212°F.

- **(a)** Derive the formulas for converting from Fahrenheit to Celsius and back.
- **(b)** What is absolute zero on the Fahrenheit scale?

Problem 1.2. The Rankine temperature scale (abbreviated °R) uses the same size degrees as Fahrenheit, but measured up from absolute zero like kelvin (so Rankine is to Fahrenheit as kelvin is to Celsius). Find the conversion formula between Rankine and Fahrenheit, and also between Rankine and kelvin. What is room temperature on the Rankine scale?

Problem 1.3. Determine the kelvin temperature for each of the following:

- **(a)** human body temperature;
- **(b)** the boiling point of water (at the standard pressure of 1 atm);
- **(c)** the coldest day you can remember;
- **(d)** the boiling point of liquid nitrogen (−196°C);
- **(e)** the melting point of lead (327°C).

Problem 1.4. Does it ever make sense to say that one object is "twice as hot" as another? Does it matter whether one is referring to Celsius or kelvin temperatures? Explain.

Problem 1.5. When you're sick with a fever and you take your temperature with a thermometer, approximately what is the relaxation time?

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