

# Thermal physics in the introductory physics course: Why and how to teach it from a unified atomic perspective

Frederick Reif<sup>(a)</sup>

Center for Innovation in Learning and Department of Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

(Received 7 April 1999; accepted 11 June 1999)

Heat and thermodynamics are traditionally taught in the introductory physics course from a predominantly macroscopic point of view. However, it is advantageous to adopt a more modern approach that systematically builds on students' knowledge of the atomic structure of matter and of elementary mechanics. By focusing on the essential physics without requiring more than elementary classical mechanics, this approach can be made sufficiently simple to be readily teachable during five or six weeks of an ordinary calculus-based introductory physics course. This approach can be highly unified, using atomic considerations to infer the properties of macroscopic systems while also enabling thermodynamic analyses independent of specific atomic models. Furthermore, this integrated point of view provides a deeper physical understanding of basic concepts (such as internal energy, heat, entropy, and absolute temperature) and of important phenomena (such as equilibrium, fluctuations, and irreversibility). © 1999 American Association of Physics Teachers.

## I. INTRODUCTION

Thermal physics (heat and basic thermodynamics) has traditionally been a part of the introductory college-level physics course. Not only does this topic deal with the macroscopic systems most commonly observed in everyday life, but it is also centrally important in the chemical, biological, and engineering fields of primary interest to many students. Furthermore, it is increasingly relevant to present-day scientific and practical concerns with the behavior of complex systems ranging from novel properties of condensed matter to environmental issues.

But how can thermal physics best be taught in an introductory physics course? This question is addressed in the present article. In particular, Sec. II points out several reasons why it is advantageous to teach the subject from a modern atomistic perspective rather than from the more traditional macroscopic point of view. Section III discusses a simple approach whereby this perspective can be implemented in a way suitable for first-year students in an introductory physics course. Finally, Sec. IV summarizes the benefits and limitations entailed by this approach.

## II. MACROSCOPIC VERSUS ATOMISTIC APPROACH

### A. Traditional macroscopic approach

Thermal physics, following historical lines of development, has traditionally been taught from a predominantly macroscopic point of view. Thus basic concepts (such as heat and entropy) are introduced largely on the basis of macroscopic considerations and only some scattered attempts are made to relate them to atomic processes.

This macroscopic approach is not easy for students because it is rather abstract and provides no readily visualizable mental models. Thus concepts such as heat, internal energy, absolute temperature, and entropy remain abstractly descriptive and largely phenomenological. The emphasis on underlying mechanisms, so prevalent in the rest of the introductory physics course, seems strangely absent in this discussion of

thermal physics. The newly introduced concepts lack a strong integrating framework and the fundamental significance of absolute temperature or entropy remains obscure.

### B. Advantages of an atomistic approach

An alternative instructional approach, considering macroscopic systems from a microscopic atomic point of view, offers the following advantages.

(1) *Highly unified approach.* It provides a highly unified approach explicitly relating the macroscopic and atomic points of view and showing how they are complementary. In particular, the approach can be based on only two fundamental ideas—(a) that all macroscopic systems consist of atomic particles and (b) that their properties can be understood by using some basic knowledge of mechanics and some simple probability considerations. The approach leads to all the purely macroscopic relationships and reasoning processes encountered in the traditional approach. But it also provides much deeper insights, making clear connections to atomic knowledge and indicating how such knowledge can be used to infer the properties of macroscopic systems.

(2) *Modern point of view.* The approach reflects a more modern point of view which builds on present-day knowledge of the atomic structure of matter and is more in tune with the kinds of thinking prevalent in contemporary physics and other scientific fields.

(3) *Greater interest to students.* The approach is more interesting to many students. Instead of dealing with the seemingly mundane questions of heat and temperature, it shows how underlying atomic processes can provide an understanding of many commonly observed macroscopic phenomena. Furthermore, this understanding can directly build on the knowledge of mechanics that students have previously acquired in their course.

(4) *Introduction to widely useful ideas.* Instead of dealing mostly with thermodynamic arguments, the atomistic approach introduces some important ideas useful to students in their future studies. (a) It introduces some basic probability notions that are widely relevant in statistics, in the analysis

of experimental results, in quantum mechanics, and in many other domains. (b) It not only derives and applies the model-independent laws of thermodynamics, but also relates them to atomic processes and statistical physics. Hence, the approach introduces ideas that prepare students to deal with future courses in thermodynamics, statistical mechanics, physical chemistry, and other fields.

### C. Instructional feasibility of an atomistic approach

The central challenge is to formulate the atomistic approach in a manner that reveals its essential insights and purely macroscopic implications, but that is sufficiently simple to be readily accessible to students in an introductory college-level physics course.

My earlier attempts<sup>1,2</sup> to reformulate the atomistic approach in simpler ways presupposed a knowledge of quantum mechanics. However, further reflection convinced me that the introduction of thermal physics could be further simplified, both to clarify the underlying physics and to make the subject readily comprehensible to much less well-prepared students. In particular, it seems possible to simplify the discussion in some of the following ways.

(1) Instead of requiring a prior knowledge of quantum physics, one can build on the basic ideas of classical mechanics learned by students at the very beginning of their introductory physics course. Although a classical discussion has some limitations compared to a more correct quantum-mechanical treatment, it is sufficient to yield almost all the important reasoning processes and results. Furthermore, most of these results require only a slight reinterpretation after students have become familiar with quantum mechanics.

(2) It is sufficient to introduce the basic notion of a probability, but quite unnecessary to discuss binomial or Gaussian distributions.

(3) Qualitative discussions can often help to introduce more quantitative considerations. Some formal mathematical derivations can also be replaced by more insightful physical arguments.

*Instructional experience in introductory physics.* These considerations led me, about 20 years ago, to use the atomistic approach to teach thermal physics in the usual calculus-based introductory physics course. The first semester of that course dealt mostly with mechanics and devoted the last five or six weeks to thermal physics. Instead of following the textbook by Halliday and Resnick,<sup>3</sup> I then taught this subject from an atomistic perspective and provided students with some special instructional materials prepared by me.

Several years of successively refined teaching efforts led me to the conclusion that I could realize the previously mentioned advantages of the atomistic approach, and yet preserve practically all the macroscopic results and reasoning traditionally taught in thermal physics. Furthermore, my experience indicated that students did not find the atomistic approach more difficult than the traditional approach or than the classical mechanics studied by them during the earlier part of the course.

## III. SIMPLE ATOMISTIC APPROACH TO THERMAL PHYSICS

Students already know that matter consists of atoms and molecules. They need only the following other modest prerequisites: (a) some rudimentary knowledge about classical

mechanics (for example, knowledge about position and velocity, about kinetic and potential energy, and about the energy law); (b) some basic mathematical knowledge about natural logarithms and simple derivatives and integrals.

Needless to say, the atomistic approach must be carefully formulated so that it is sufficiently simple to be comprehensible to first-year students, yet provides them with significant abilities to explain or predict important phenomena. In the rest of this section I outline such a pedagogical formulation of the atomistic approach and try to do so in sufficient detail that it can be readily imitated by other instructors.<sup>4</sup>

### A. Macroscopic versus atomistic descriptions

#### 1. Macroscopic description

The solids, liquids, gases, and other systems observed by us in everyday life are large scale or “macroscopic,” that is, very large compared to the size ( $10^{-10}$  m) of a typical atom or molecule. Such a system can be described by relatively few macroscopically measurable quantities. (For example, a gas or liquid in a time-independent equilibrium situation can be adequately described by its volume and pressure.)

#### 2. Atomistic description

We also know that a macroscopic system consists of a very large number (of the order of  $10^{24}$ ) atoms or molecules. Instead of describing such a system from a macroscopic point of view, we may also describe it from an atomistic point of view that focuses attention on every atomic particle in the system. For example, we might do so by specifying the position and velocity of every particle in the system. Correspondingly, the atomistic description<sup>5</sup> would be very complex, requiring the specification of something like  $10^{24}$  quantities.

#### 3. Relation between descriptions

What is the relation between the macroscopic and atomistic descriptions? In particular, we know that all matter consists of only a few kinds of atomic particles—and we also know something about the laws of mechanics describing the motions and interactions of such particles. How can this basic knowledge help us to explain or predict the observable properties of the diverse macroscopic systems commonly encountered by us? This is a central question that we wish to answer in our study of physics.

### B. Thermodynamic energy law

#### 1. Energy law of mechanics

The energy law of mechanics, applied to any system of particles, can be written as

$$\Delta E = W_{\text{ext}}, \quad (1)$$

where  $E = K + U$  is the “internal energy” of the system (that is, its energy when its center of mass is at rest). Here  $K$  is the total kinetic energy of all the particles in the system, and  $U$  is the total potential energy of interactions among all these particles. The external work  $W_{\text{ext}}$  is the work done on the system by all external interactions not included in this potential energy.

## 2. Thermodynamic energy law

This external work can be decomposed into some macroscopic work  $W_{\text{mac}}$  and some remaining nonmacroscopic work  $W_{\text{nonmac}}$ . Thus Eq. (1) can be expressed in the form

$$\Delta E = W_{\text{mac}} + W_{\text{nonmac}}. \quad (2)$$

The *macroscopic* work  $W_{\text{mac}}$  (done on the system by some macroscopically measurable force moving through some macroscopically measurable distance) can simply be called the work  $W$  on the system. The remaining nonmacroscopic work  $W_{\text{nonmac}}$  (done, because of atomic interactions, on particles in the system by neighboring particles outside the system) is conventionally called the heat  $Q$  absorbed by the system.<sup>6</sup> With these definitions the relation (2) becomes the “thermodynamic energy law”

$$\Delta E = W + Q, \quad (3)$$

which is historically called the “first law of thermodynamics.”<sup>7</sup>

The macroscopic work  $W$  can be readily determined by macroscopic measurements. But how can such macroscopic measurements be used to determine the internal energy  $E$  and heat  $Q$ , quantities that are so closely related to atomic particles and their interactions?

## 3. Useful analogy

These issues can be clarified by the following analogy.<sup>8</sup> The amount  $A$  of water in a lake can change either (a) because of the flow  $F$  of water into the lake from some streams or (b) because of the condensation  $C$  of water from moisture in the surrounding air.<sup>9</sup> Thus the change in the amount of lake water is equal to

$$\Delta A = F + C. \quad (4)$$

This relation is analogous to the thermodynamic energy law (3). Here the flow  $F$  of water from streams is readily visible and measurable. But how can one measure the other two quantities  $\Delta A$  and  $C$ ?

This measurement can be done because one can separately eliminate flow (for example, by closing dams in the streams) or eliminate condensation (for example, by covering the lake with a water-impermeable cover). Thus one can do the following. (a) Any level indicator (for example, some arbitrarily shaped stick inserted into the bottom of the lake) can be used to indicate changes in the water level and thus corresponding changes in the amount of water in the lake. (b) Condensation can be eliminated by covering the lake with an impermeable cover.<sup>10</sup> Under these conditions one can determine the change of water level corresponding to any measurable amount of water flow into the lake (that is, corresponding to any change  $\Delta A$  in the amount of water in the lake). (c) After this calibration, a measured change in water level can be used to determine the corresponding change  $\Delta A$  in the amount of water in the lake, even in the general situation where no cover is in place. But in this case the change  $\Delta A$  may also be due to condensation and, according to Eq. (4), this condensation  $C = \Delta A - F$ . Thus the condensation can be found by simple subtraction.

## 4. Measurability of internal energy and heat

Similarly, one can separately eliminate any work done on a macroscopic system (for example, by suppressing any mac-

roscopic motion in the presence of a macroscopic force) or eliminate any absorbed heat [for example, by covering the system with an “adiabatic” (that is, thermally insulating) cover]. Thus one can do the following. (a) Any arbitrary thermometer (for example, a mercury thermometer or electrical thermometer) can be used to indicate changes in the system’s internal energy. (b) Heat transfer can be eliminated by covering the system with an adiabatic cover.<sup>11</sup> Under these conditions one can determine the change of thermometer indication (“temperature”) corresponding to any measurable amount of work done on the system, that is, corresponding to any change  $\Delta E$  of the system’s internal energy. (c) After this calibration, a measured change in thermometer indication can always be used to determine the corresponding change  $\Delta E$  of the system’s internal energy, even in the general situation where no adiabatic cover is in place. But in this case the change  $\Delta E$  may also be due to absorbed heat and, according to Eq. (3), this heat  $Q = \Delta E - W$ . Thus the absorbed heat can be found by simple subtraction.

## 5. Applications of the thermodynamic energy law

Any system in a time-invariant macroscopic equilibrium situation (“macrostate”) has some well-specified internal energy. When a system changes from one situation to another, its internal energy changes by a definite amount  $\Delta E$  independent of the process producing this change. However, different processes (involving different amounts of work  $W$  and heat  $Q$ ) can be used to achieve a change between the same two situations. The thermodynamic energy law (3) then implies that the sum  $W + Q$  must be the *same* for any such process.

All applications of the thermodynamic energy law exploit this basic conclusion. Correspondingly, students can be given all of the usual illustrative problems and examples discussed in a conventional macroscopic approach to thermodynamics.<sup>12</sup>

## C. Statistical description of macroscopic systems

### 1. Statistical description

In many cases it is practically (or theoretically) impossible to make definite predictions about the behavior of a system. For example, one cannot definitely predict the result of tossing a pair of coins or winning a jackpot, nor can one definitely predict when someone will die or get into an automobile accident.

However, in such cases one may still be able to predict the *probabilities* of various events, that is, one may still be able to make *statistical predictions*. Indeed, such predictions are often of great practical utility (for example, in gambling or the insurance business).

A statistical description of a system requires the following four basic ingredients (all of which can be illustrated in the simple case of a pair of tossed coins).

(1) *Specification of possible states.* One must be able to specify the possible results obtained by observing the system. (For example, in the case of the pair of tossed coins, each coin can display either heads or tails. Hence, this system can be in any one of four possible states.)

(2) *Statistical assembly of systems.* Instead of considering a single system, one can consider an assembly (or “ensemble”) of a very large number  $\mathcal{N}$  of similar systems subject to similar conditions. If  $\mathcal{N}_r$  of these systems are in a

particular state  $r$ , the fraction  $P_r = \mathcal{N}_r / \mathcal{N}$  of systems in this state is called the “probability” of finding a system in this state.

Although one may not be able to predict the outcome of an experiment on a single system, one may still be able to predict the *probability* of the outcome occurring in such a statistical assembly of similar systems. (For example, although one cannot predict the outcome of tossing one particular pair of coins, one may still be able to predict the probability of any outcome resulting from tossing many such pairs of coins.)

(3) *Statistical postulate.* To predict such probabilities, one must formulate a basic assumption (or “postulate”) serving as the basis of all such theoretical predictions. (For example, in the case of the pair of tossed coins, one might assume that all possible states occur with equal probability.)

(4) *Statistical predictions.* The statistical postulate can be used to calculate the probabilities of various outcomes. A successful statistical theory is one for which these calculated predictions agree with the observed probabilities.<sup>13</sup>

## 2. Statistical theory of macroscopic systems

A macroscopic system consists of a very large number of atomic particles. A detailed consideration of the motions and interactions of all these particles would be a hopelessly complex task. However, a less detailed statistical consideration can be relatively simple and effective. The needed ingredients are the following (similar to those previously illustrated with the pair of tossed coins).

(1) *Specification of possible states.* The “basic state” of a system<sup>14</sup> (that is, its state described from an atomistic point of view) can be specified by the position and velocity of *every one* of its atomic particles.<sup>15</sup> Thus one needs to specify an enormous number of quantities, the three position coordinates ( $x, y, z$ ) of every particle, and its three velocity components ( $v_x, v_y, v_z$ ).<sup>16</sup>

The description can be somewhat simplified by “digitizing” the position coordinates and velocity components, that is, by replacing these continuous quantities by discrete integral values (each of which denotes any of the values lying in a small range determined by the desired accuracy of description).<sup>17</sup> This digitizing makes the possible basic states of a system discrete and countable.

(2) *Statistical assembly of systems.* Instead of focusing attention on a single system, consider probabilities of occurrence in a statistical assembly of a large number  $\mathcal{N}$  of similar such systems. (For example, instead of focusing attention on a single container of gas, consider an assembly of many such containers.) The aim is to predict such probabilities theoretically.

(3) *Statistical postulate.* Nothing in the laws of mechanics suggests that a system should be preferentially in any one of its possible basic states rather than in any other. Similarly, repeated tossing of a set of coins will ultimately lead to a situation where they are equally likely to be found in any one of their possible states. Such considerations suggest the following basic assumption or “statistical postulate:” *The probabilities of finding an isolated macroscopic system in its possible basic states change with time until the system reaches a time-independent equilibrium situation where these probabilities are equal.*

(4) *Statistical predictions.* The statistical postulate allows one to make quantitative predictions about probabilities in an

equilibrium situation and to make qualitative predictions about the approach to equilibrium. The entire remaining discussion of macroscopic systems will be based on this postulate.

## D. Qualitative properties of macroscopic systems

### 1. Equilibrium situation

*a. Probability of an equilibrium situation.* When a macroscopic system is in a particular situation (or “macroscopic state”)  $A$ , it can be found in any one of a large number  $\Omega_A$  of possible basic states (compared to the total number  $\Omega_{\text{tot}}$  of possible basic states available to the system in *all* situations). According to the statistical postulate, the probability  $P_A$  that the system in equilibrium is found in the situation  $A$  is then

$$P_A = \Omega_A / \Omega_{\text{tot}} \propto \Omega_A, \quad (5)$$

that is, it is proportional to the number  $\Omega_A$  of basic states in  $A$ .

*b. Example of a simple gas in equilibrium.* A gas, consisting of  $N$  molecules in a box, can serve as an instructive example. The position of each molecule can be adequately specified by indicating whether it is in the left or right half of the box. Thus each molecule can be in two basic states. The total number  $\Omega_{\text{tot}}$  of possible states for the entire gas of  $N$  molecules is then  $2 \times 2 \times 2 \times \dots = 2^N$ . The probability  $P_n$  of a situation, where  $n$  of these molecules are in the left half of the box, can then be found merely by counting the number of possible basic states in this situation.

For example, for a gas of 4 molecules, the probabilities that 0, 1, 2, 3, or 4 molecules are in the left half of the box are 1/16, 4/16, 6/16, 4/16, and 1/16. The students can similarly be asked to count the number of possible states (and to list the corresponding probabilities) for a gas of 5 or 6 molecules. Furthermore, one can show them graphs illustrating the probability distributions obtained for a gas consisting of a larger number of molecules (such as  $N=40$ ).<sup>18</sup>

*c. General conclusions.* The preceding examples are sufficient to arrive at the following general conclusions. (a) The most probable situation is one where there are an equal number of molecules in both halves of the box (because this situation corresponds to the largest number of possible ways that the molecules can be distributed between the two halves). (b) Situations where the number of molecules in the two halves are quite different are highly improbable. (For instance, an extreme situation where *no* molecule is in the left half of the box can be realized in only one way and is thus exceedingly unlikely.) (c) When the total number  $N$  of molecules is large (especially, in realistic gases where  $N \approx 10^{24}$ ), situations where the molecules are nearly equally distributed between the two halves of the box are overwhelmingly more probable than any others.

### 2. Fluctuations in equilibrium

The preceding example indicates that the number  $n$  of molecules in one half of the box is not always exactly equal to  $N/2$ , but may slightly deviate from this value. Deviations (“fluctuations”) that are appreciable compared to  $N$  itself are, however, very improbable when the total number  $N$  of molecules is large.

Indeed, small fluctuations are always present in the case of *any* macroscopic system in equilibrium. But these fluctua-

tions are ordinarily observable only if one tries to make very precise observations or deals with sufficiently small systems.<sup>19</sup>

### 3. Approach to equilibrium

According to the statistical postulate of Sec. III C 2, any isolated macroscopic system will change until it reaches an unchanging equilibrium situation. However, the postulate makes *no* quantitative statement about the *time* required to reach equilibrium. (The calculation of such a time would require much more detailed analyses.)

For example, suppose that a gas is initially in the left half of a box divided by a partition into two equal parts. If a hole is made in the partition, the gas will ultimately always reach an equilibrium situation where approximately half the molecules are in either part of the box. But the time required to reach this equilibrium situation will be longer if the hole is small than if it is large.

### 4. Irreversibility

*a. Reversible and irreversible processes.* Because a macroscopic system tends to approach an equilibrium situation, it is possible to specify a preferred direction of time and thus to distinguish the future from the past. More precisely, imagine that one makes a movie of a process. If one can distinguish whether the movie is run through a projector forward or backward, then one has identified a special direction of time and the process is called “irreversible.” But if one *cannot* tell whether the movie is run through this projector forward or backward, then one has *not* identified a special direction of time and the process is called “reversible.”

*b. Example of irreversibility in a gas.* For example, consider the process where a gas, initially entirely confined in the left half of a box, spreads throughout the entire box until it reaches equilibrium where nearly an equal number of molecules are in the two halves. If a movie of this process is played backward through a projector, it would show the gas molecules, initially uniformly distributed throughout the entire box, spontaneously all moving into the left half of the box. Such a process would never be observed in reality. Hence one could immediately tell that the movie is being played backward and that the originally filmed process is irreversible.

*c. Irreversibility and probabilities.* Strictly speaking, the reverse process (where the gas becomes all concentrated in the left half) is not impossible, just exceedingly improbable. For example, all the molecules in the right half of the box might possibly *all* be moving to the left at a particular instant. But, in the case of some  $10^{24}$  molecules, such a spontaneous fluctuation would occur with utterly negligible probability.

To show that there is no sharp distinction between irreversible and reversible processes, consider a gas which consists of only 4 molecules in a box. A spontaneous fluctuation, where all molecules are in the left half, would then (in equilibrium) occur with a probability of  $1/16$ . Hence, it would be large enough to be readily observed. If a movie showed this gas concentrating in the left half of a box, one would then *not* be able to tell whether this movie is being played forward or backward. Thus this process would seem reversible.<sup>20</sup>

*d. Other examples.* Students can be shown many other examples. For instance, they can be asked to judge the reversibility of processes involving only a few particles (for

example, planets moving around the sun) and of processes involving various macroscopic systems (for example, a bouncing ball coming to rest or a chicken crawling out of an egg).

## E. Number of basic states and entropy

### 1. Basic states and macroscopic parameters

Probabilities can be calculated from Eq. (5) if one knows the number of basic states available to a macroscopic system. But how does the number  $\Omega$  of such basic states depend on the macroscopic parameters describing a system, for example, on its volume  $V$  or internal energy  $E$ ? This question can be readily answered in the simple case of an ideal monatomic gas of  $N$  molecules. (A gas is considered “ideal” if its intermolecular interactions contribute negligibly to its internal energy.)

*a. Dependence of  $\Omega$  on volume.* Suppose that the volume  $V$  of the gas container were 2 times larger. Then 2 times as many possible (digitized) positions would be available to each molecule, and hence  $2 \times 2 \times 2 \times \dots = 2^N$  times as many positions to all the  $N$  molecules. More generally, the number  $\Omega$  of possible basic states depends then on the volume so that

$$\Omega \propto V^N. \quad (6)$$

*b. Dependence of  $\Omega$  on kinetic energy.* Similarly, suppose that the kinetic energy  $K$  of the gas were 2 times larger. On average, the contribution  $m v_x^2/2$  to the kinetic energy of a molecule’s velocity component  $v_x$  would then be 2 times larger. Hence  $v_x$  would be  $2^{1/2}$  times larger so that the number of possible (digitized) basic states corresponding to it would also be  $2^{1/2}$  times larger. Because there are  $3N$  such velocity components, the total number of basic velocity states available to all the  $N$  molecules would then be  $2^{1/2} \times 2^{1/2} \times 2^{1/2} \times \dots = 2^{3N/2}$  times larger. More generally, the number  $\Omega$  of possible basic states depends then on the kinetic energy  $K$  of the gas so that

$$\Omega \propto K^{3N/2}. \quad (7)$$

*c. Qualitative conclusions.* Because  $N \approx 10^{24}$ , the exponents in (6) and (7) are extremely large. Hence, the number of possible basic states increases exceedingly rapidly as the volume  $V$  or kinetic energy  $K$  of the gas becomes larger.

### 2. Basic entropy

Because the number  $\Omega$  of basic states is extremely large and rapidly increasing, it is much more convenient to work with its logarithm,

$$\sigma = \ln \Omega, \quad (8)$$

which is much less large and less rapidly increasing. The quantity  $\sigma$  may be called the “basic entropy” of a system.

The basic entropy provides a measure of a system’s randomness. A situation which can be realized in many different ways is considered more random than one which can be realized in only a few ways. For example, a situation where the molecules of a gas are anywhere within a box can be realized in many more ways than one where they are all in only one half of the box; hence it is a more random situation. Similarly, a hand consisting of any 13 red cards is more random than a hand consisting only of diamonds (a situation that can be realized in only one way).

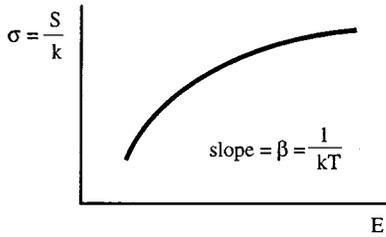


Fig. 1. Qualitative dependence of a system's entropy on its internal energy.

### 3. Properties of the entropy

*a. Dependence of entropy on internal energy.* Consider a system of fixed volume. If it is a monatomic ideal gas of  $N$  molecules, its internal energy  $E = K$  because its potential energy  $U$  is negligible. The basic entropy of this gas is, by Eq. (7), equal to

$$\sigma_{\text{ideal gas}} = \ln \Omega = \text{constant} + (3N/2) \ln E. \quad (9)$$

A more complex macroscopic system (such as a liquid or a solid) has not only kinetic energy, but also an appreciable potential energy due to the mutual interactions of its constituent atomic particles. The basic entropy  $\sigma$  of such a system depends on its internal energy  $E$  in a way that is more complicated than in Eq. (9), but also increases with its internal energy, roughly in the manner indicated by the graph in Fig. 1.

*b. Entropy gradient.* When a system's internal energy changes by a small amount  $dE$ , its basic entropy changes by a corresponding small amount  $d\sigma$ . The quantity

$$\beta = d\sigma/dE \quad (10)$$

describes how rapidly the system's basic entropy changes with increasing energy. It can be called the "entropy gradient" and specifies the slope of the graph in Fig. 1.

*c. Entropy and absolute temperature.* For historical reasons (and partly for ease of measurement) it is convenient to introduce two other quantities closely related to the fundamental quantities  $\sigma$  and  $\beta$ . Thus the quantity  $S$ , simply called "entropy," is defined so that

$$S = k\sigma = k \ln \Omega \quad (11)$$

and the quantity  $T$  is defined so that

$$T = 1/(k\beta). \quad (12)$$

The quantity  $T$  is called the "absolute temperature," for reasons clarified in the next section. The value of the constant  $k$  ("Boltzmann's constant") will be discussed later and depends on international conventions about measurement standards.

*d. Energy dependence of  $\beta$  or  $T$ .* The quantity  $\beta$ , specifying the slope of the graph in Fig. 1, is positive and decreases with increasing internal energy. Correspondingly, the absolute temperature  $T$  is also positive, but increases with increasing internal energy.<sup>21</sup>

The definitions (10) and (12) imply that the quantity  $kT$  has the units of energy and that

$$d\sigma = \beta dE \quad \text{or} \quad dS = dE/T. \quad (13)$$

*e. Entropy of a composite system.* Consider a macroscopic system  $X^*$  consisting of two macroscopic parts  $X$  and  $X'$ . If  $X$  is in a particular basic state,  $X'$  can then be in any

one of its  $\Omega'$  possible basic states. But because  $X$  itself can be in any one of its  $\Omega$  possible basic states, the total number  $\Omega^*$  of basic states available to the entire system  $X^*$  is

$$\Omega^* = \Omega \Omega'. \quad (14)$$

Because the corresponding logarithms of these quantities are additive, the entropies of these systems are also additive. Thus

$$\sigma^* = \sigma + \sigma' \quad \text{or} \quad S^* = S + S'. \quad (15)$$

### F. Thermal interaction

Consider two macroscopic systems  $X$  and  $X'$  which are in contact so that they can exchange energy in the form of heat, but do not do any macroscopic work. (For example, the volume of each system remains fixed.) If the composite system  $X^*$  is isolated, its internal energy  $E^*$  remains constant. Thus the energies  $E$  and  $E'$  of the two systems must satisfy the relation

$$E + E' = E^* = \text{constant}. \quad (16)$$

The energy of each system can then have any value, but changes of the systems' energies must be related so that

$$\Delta E' = -\Delta E. \quad (17)$$

#### 1. Thermal equilibrium

*a. Probability of a particular energy distribution.* Suppose that two systems are in equilibrium. What is the probability  $P(E)$  of a situation where the system  $X$  has an energy  $E$  (while the other system  $X'$  has the remaining energy  $E' = E^* - E$ )?

According to Eq. (5), this probability must be proportional to the number  $\Omega^*$  of basic states available to the total system  $X^*$  when  $X$  has the energy  $E$ . Hence Eqs. (14) and (15) imply that

$$P(E) \propto \Omega^* = \Omega(E) \Omega'(E'), \quad (18)$$

or

$$\ln P(E) = \text{constant} + \sigma^* = \text{constant} + \sigma(E) + \sigma(E'). \quad (19)$$

*b. Most probable situation.* The number of basic states is an extremely rapidly increasing function of the energy. As the energy  $E$  increases and  $E'$  correspondingly decreases, the factor  $\Omega(E)$  in Eq. (18) increases extremely rapidly while the factor  $\Omega'(E')$  decreases extremely rapidly. The result is an extremely sharp maximum in the probability  $P(E)$ , or a correspondingly less sharp maximum in its logarithm.<sup>22</sup> At this maximum  $\ln P(E)$  does not change if the energy  $E$  changes by an infinitesimal amount  $dE$ . Hence Eq. (19) implies that the maximum occurs when

$$0 = d\sigma/dE + d\sigma'/dE = d\sigma/dE - d\sigma'/dE' = \beta - \beta'$$

so that

$$\beta = \beta' \quad \text{or} \quad T = T'. \quad (20)$$

In equilibrium, the most probable situation is thus one where the energy  $E$  of the system  $X$  has a value  $E_{\text{eq}}$  such that the absolute temperatures  $T$  and  $T'$  of the systems are equal.<sup>23</sup> (As usual, very small energy fluctuations occur with lower probabilities around this equilibrium value of the en-

ergy.) The equality of temperatures in thermal equilibrium indicates that  $T$  has the properties of a temperature and motivates its name “absolute temperature.”

## 2. Approach to thermal equilibrium

If the absolute temperatures of the systems  $X$  and  $X'$  are initially *not* equal, they will not be in equilibrium when brought into contact with each other. Hence, they will exchange energy until they reach equilibrium. Except for very small fluctuations, they will then reach the most probable situation where the entropy  $S^*$  of the entire system is maximum and where the absolute temperatures  $T$  and  $T'$  are equal.

The entropy  $S^*$  of the entire system thus increases in the process of reaching equilibrium. Also Eq. (17) indicates that the internal energy of one system increases while the energy of the other one decreases. The system which gains energy (that is, which absorbs positive heat) is called the initially “colder” system. The system which loses energy (that is, which absorbs negative heat or, equivalently, gives off positive heat) is called the initially “warmer” system.

As pointed out in Sec. III E 3, a system’s absolute temperature increases as its internal energy increases. Hence the system which gains energy (the “colder” system) goes to a higher absolute temperature while the system which loses energy (the “warmer” system) goes to a lower absolute temperature. Hence *heat flows from the system at the higher absolute temperature to the system at the lower absolute temperature.*<sup>24</sup> The absolute temperature provides, therefore, information about the direction of heat flow occurring between two systems in thermal contact.

## 3. Mutual equilibrium among several systems

If a system  $X$  is in thermal equilibrium with another system  $X'$ , then Eq. (20) implies that  $T=T'$ . Similarly, if  $X$  is in equilibrium with a third system  $X''$ , then Eq. (20) implies that  $T=T''$ . These results lead to the mathematical conclusion that  $T'=T''$ . The corresponding physical conclusion can be summarized by the following statement (called the “zeroth law of thermodynamics”): *If two systems are each in thermal equilibrium with a third system, they will be in thermal equilibrium with each other.*

This statement indicates why any arbitrary thermometer (such as a mercury thermometer) can be used to decide whether two systems will, or will not, be in equilibrium when brought into contact with each other. If the thermometer readings are the same when the thermometer is applied to the two systems, then the systems will be in equilibrium when brought into contact with each other. But otherwise they will not.

## G. Ideal gases and temperature measurement

### 1. Properties of ideal gases

*a. Energy of a monatomic ideal gas.* In a *monatomic* ideal gas of  $N$  molecules, the internal energy  $E$  of the gas is just the total kinetic energy  $K$ . The basic entropy  $\sigma$  of the gas depends on its energy  $E$  in the manner specified by Eq. (9). Hence  $\beta = d\sigma/dE = 3N/(2E)$  so that

$$E = K = (3/2)N/\beta = (3/2)NkT. \quad (21)$$

*b. Energy of a polyatomic ideal gas.* If a gas consists of  $N$  *polyatomic* molecules, the internal energy  $E$  of the gas

consists of the kinetic energy  $K_{c.m.}$  due to the center-of-mass motions of these molecules and the intramolecular energy  $E_{intra}$  due to the atoms moving relative to the center of mass of each molecule. Thus

$$E = K_{c.m.} + E_{intra}. \quad (22)$$

The system involving the center-of-mass motions of the molecules, and the system involving the motions of atoms within the molecules, can exchange energy with each other. According to Eq. (20), these systems are characterized by the same absolute temperature  $T$ . Furthermore, the center-of-mass kinetic energy  $K_{c.m.}$  is related to the temperature  $T$  in the same way specified by (21) for a monatomic gas without any intramolecular motions.

*c. Dependence of internal energy on volume.* The internal energy  $E$  of a gas depends ordinarily on its volume and temperature. In an *ideal* gas the molecules are sufficiently far apart that their mutual potential energy of interaction  $U$  contributes negligibly to their total energy. Hence  $U$  is unaffected if the volume of the container is changed (so that the average separation between molecules is changed). The *intramolecular* energies also do not depend on the separation between the molecules. Hence the internal energy  $E$  of an *ideal* gas does *not* depend on its volume, but only on its temperature:

$$E = E(T) \text{ independent of } V. \quad (23)$$

*d. Ideal gas law.* Familiar kinetic-theory arguments can be used to calculate the pressure  $p$  produced by an ideal gas as a result of molecular collisions. Thus it can be shown that

$$p = (2/3)nK_1, \quad (24)$$

where  $n$  is the number of molecules per unit volume and  $K_1$  is the average center-of-mass kinetic energy of a molecule. Since Eq. (21) implies that  $K_1 = K/N = (3/2)kT$ , Eq. (24) then yields the relation

$$p = nkT. \quad (25)$$

Because  $n = N/V$ , Eq. (25) can also be expressed in the equivalent forms

$$pV = NkT \text{ or } pV = \nu RT, \quad (26)$$

where  $\nu$  is the number of moles of the gas and the “gas constant”  $R = N_A k$  (where  $N_A$  is Avogadro’s number). The relation (26) connecting the pressure, volume, and absolute temperature is the “ideal gas law.”

## 2. Measurement of absolute temperature

*a. Measurement of  $kT$ .* The relation (26) allows one to measure  $kT$ , that is, the entropy gradient  $\beta = (kT)^{-1}$  of an ideal gas. This measurement can be done by determining the pressure  $p$  of the gas, its volume  $V$ , and the number  $N$  of molecules in it.

Suppose that the gas is in equilibrium when in thermal contact with some other system. According to Eq. (20), the entropy gradient  $\beta$  of the system is then the same as that of the gas. Hence an ideal gas can be used as a thermometer to measure the entropy gradient  $\beta$  of *any* other system.

*b. Kelvin temperature scale.* It is somewhat difficult to determine the number  $N$  of molecules in a gas. But the ratio of two absolute temperatures can be found without needing to know this number. Indeed, suppose that one uses a

“constant-volume gas thermometer” where the volume of the gas is kept fixed. Then Eq. (26) implies that

$$T/T' = p/p', \quad (27)$$

that is, the ratio of two absolute temperatures is equal to the readily measurable ratio of the corresponding pressures of the gas.

Hence, all absolute temperatures can be easily determined by comparison with some easily reproducible standard temperature. By international convention, this standard temperature is chosen to be the one where water is at its “triple point” (that is, in the situation where water coexists in equilibrium in its liquid, solid, and gaseous forms). Furthermore, this convention *defines* the absolute temperature  $T_t$  of water at the triple point to be exactly

$$T_t = 273.16 \text{ kelvin} \quad (28)$$

by introducing the unit “kelvin” (abbreviated by “K”). This particular numerical value was chosen so that this temperature scale agrees closely with earlier temperature scales. All other temperature scales (like the Celsius or Fahrenheit scales) are nowadays defined in terms of the kelvin temperature scale.

*c. Determination of Boltzmann’s constant.* The value of Boltzmann’s constant  $k$  can be found by combining a measurement of  $\beta = (kT)^{-1}$  with a measurement of the absolute temperature  $T$  expressed in terms of the unit kelvin. Thus one finds that (approximately)

$$k = 1.38 \times 10^{-23} \text{ J/K}. \quad (29)$$

Correspondingly, the gas constant  $R = N_A k$  has the approximate value 8.31 J/(K mol).

*d. Importance of the absolute temperature.* Determinations of the absolute temperature (for example, by means of an ideal-gas thermometer) are important for the following reasons. (a) As pointed out in Sec. III F 2, the absolute temperature is directly related to the direction of heat flow between systems in thermal contact. (b) A measurement of the absolute temperature of a system provides significant atomic information about how the number of its basic states changes with its energy. (c) Most properties of macroscopic systems are temperature dependent and theoretical calculations of such properties are always expressed in terms of the absolute temperature. Hence measurements of the absolute temperature are essential to use or verify theoretical predictions.<sup>25</sup>

## H. Heat capacity

The discussion of heat capacity can be similar to that in a traditional macroscopic approach to thermodynamics (and can let students deal with similar kinds of applications and problems). The following merely lists the topics that may usefully be discussed.

- (1) Definition of heat capacity  $C = d'Q/dT$  and of specific heats.<sup>26</sup>

$$Q = \int C dT = C(T_B - T_A) \quad \text{if } C = \text{constant}.$$

Definition of heat reservoir ( $C$  very large,  $T$  constant).

- (2) Heat capacity at constant volume:  $C_v = dE/dT$ .  
For a monatomic ideal gas,  $c_v = (3/2)R$  per mol.
- (3) Heat capacity at constant pressure.  
Relation between molar specific heats of an ideal gas:  
 $c_p - c_v = R$ .

- (4) Thermal interaction and calorimetry.  
Energy conservation for two interacting systems:  
 $Q + Q' = 0$ .  
Determination of temperature from known heat capacities. Experimental comparison of heat capacities.
- (5) Entropy determination from heat capacity.

$$dS = dE/T = d'Q/T = CdT/T$$

$$S_B - S_A = \int C dT/T = C \ln(T_B/T_A) \quad \text{if } C = \text{constant}.$$

- (6) Isothermal and adiabatic processes of an ideal gas.  
 $pV = \text{constant}$  and  $pV^\gamma = \text{constant}$  (where  $\gamma = c_p/c_v$ ).

## I. General thermodynamic interaction

The preceding sections discussed thermal interactions that involve no macroscopic work. Let us now examine more general interactions where such work may also be done.

### 1. Entropy change in a quasi-static process

*a. Entropy change due to bodily motion.* Suppose that a solid object is slowly moved (for example, that a weight is lifted) so that macroscopic work may be done on it. Then the system’s internal motions (relative to its center of mass) are unaffected and the system’s entropy remains correspondingly unchanged.

*b. Quasi-static adiabatic process.* Consider now *any* system (for example, a gas) whose volume can change so that macroscopic work can be done on it. For example, imagine that the system is in a container closed by a movable piston which can freely move up or down, but that the system is thermally insulated so that it does not absorb any heat from the piston or its other surroundings. Then the entropy  $S^*$  of the entire isolated system is  $S^* = S + S'$ , where  $S$  is the entropy of the system itself and  $S'$  is the entropy of the piston.

If this system is in equilibrium, it is (except for negligibly small fluctuations) in its most probable situation where the entropy  $S^*$  is maximum and the piston is at rest so that the system’s volume remains constant. Now suppose that the system’s volume is changed by a small amount (for example, that the piston is slightly moved and thus does some work on the system). If this process is carried out so slowly that the system remains extremely close to equilibrium (that is, if the process is “quasi-static”), the entropy  $S^*$  remains extremely close to its maximum so that

$$dS^* = dS + dS' = 0. \quad (30)$$

But the entropy  $S'$  of the piston does not change as a result of its bodily motion. Hence

$$dS = 0. \quad (31)$$

The entropy of a thermally insulated system remains, therefore, unchanged in a quasi-static process (even if work is done on the system).

*c. General quasi-static process.* A more general infinitesimal quasi-static process (where work  $d'W$  is done on a system and heat  $d'Q$  is also absorbed by it) can be decomposed into two successive quasi-static processes. (a) A process where no heat is absorbed, but work  $d'W$  is done. By Eq. (31) the system’s resulting entropy change is then  $dS = 0$ . (b) A process where no work is done on the system, but heat  $d'Q$  is absorbed. By (13) the resulting entropy change

of the system at the absolute temperature  $T$  is then  $dS = d'Q/T$ . The system's net entropy change is the sum of these two entropy changes. Hence in any quasistatic infinitesimal process,

$$dS = d'Q/T. \quad (32)$$

*d. Measurement of entropy change.* Suppose that a system is brought from a situation  $A$  to another situation  $B$  by means of a quasi-static process passing through a sequence of slightly differing successive equilibrium situations. Then Eq. (32) implies that

$$S_B - S_A = \int_A^B d'Q/T. \quad (33)$$

Hence, the difference between the entropies of any two situations  $A$  and  $B$  can be determined by using any quasi-static process connecting these situations. One only needs to measure the successive small heats  $d'Q$  absorbed at corresponding absolute temperatures  $T$ .<sup>27</sup>

## 2. Implications of the entropy–heat relation

*a. Entropy related to system parameters.* Relation (32) can be combined with the thermodynamic energy law (3) to yield

$$dS = (dE - d'W)/T = (dE + p dV)/T. \quad (34)$$

Useful information can, therefore, be obtained if one knows how the entropy depends on the macroscopic parameters describing a system. To be specific, Eq. (34) implies that<sup>28</sup>

$$\text{if } V = \text{constant, } dS/dE = 1/T, \quad (35)$$

$$\text{if } E = \text{constant, } dS/dV = p/T. \quad (36)$$

*b. Applications to an ideal gas.* The entropy  $S$  of an ideal gas consists of two parts so that

$$S = S_V + S_E. \quad (37)$$

The part  $S_V$ , due to the possible positions of the molecules throughout the volume  $V$  of the gas, depends on the volume  $V$  according to Eq. (6) so that

$$S_V = \text{constant} + kN \ln V. \quad (38)$$

The remaining part  $S_E$  of the entropy depends on the internal energy  $E$  (that is, on the possible center-of-mass velocities of these molecules and on any intramolecular motions), but does not depend on the volume  $V$ .

Relation (35) applied to the entropy (37) of an ideal gas yields  $dS_E/dE = 1/T$ . Because the left-hand side does not depend on the volume, this relation implies that the internal energy  $E$  of an ideal gas does not depend on its volume, but only on its absolute temperature. Thus one regains the previously obtained result (23).

Relation (36), applied to (37) and (38), yields

$$kN/V = p/T \quad \text{or} \quad pV = NkT. \quad (39)$$

Thus one regains the ideal gas law of (26), but in a very simple way that does not require examining how the pressure is produced by molecular collisions.

## 3. Summary of statistical thermodynamics

By starting from the knowledge that any macroscopic system consists of many atomic particles, we have been able to

infer the macroscopic properties of specific systems (for example, the pressure or heat capacity of an ideal gas). Furthermore, we have been able to derive the following general principles applicable to all macroscopic systems and completely independent of any detailed knowledge about their atomic constituents. (These principles, called ‘‘laws of thermodynamics,’’ were actually discovered in the nineteenth century before the atomic nature of matter was well understood.)

*a. Zeroth law of thermodynamics.* This law summarizes the result obtained in Sec. III F 3: If two systems are each in thermal equilibrium with a third system, they will be in thermal equilibrium with each other.

*b. First law of thermodynamics.* This is the thermodynamic energy law (3),

$$\Delta E = W + Q. \quad (40)$$

*c. Second law of thermodynamics.* This law specifies that the entropy of an isolated system tends to increase as the system approaches its most probable equilibrium situation. It also specifies, according to (32), how the entropy changes in any quasi-static process. Thus the law can be summarized by the following relations:

For any isolated system,

$$\Delta S \geq 0. \quad (41)$$

For any infinitesimal quasi-static process,

$$dS = d'Q/T. \quad (42)$$

*d. Statistical significance of the entropy.* The probability  $P_A$ , that a system in equilibrium is found in a situation  $A$ , is related to its entropy  $S_A$  according to (5). Thus

$$P_A \propto \exp(S_A/k). \quad (43)$$

Although this principle transcends the classical laws of thermodynamics, it is also completely macroscopic and independent of any specific knowledge about atoms.

*e. Entropy and specific atomic knowledge.* The relation  $S = k \ln \Omega$ , specified in Eq. (11), connects the entropy to atomic knowledge about the basic states of any specific system. Hence this relation allows one to calculate the macroscopic properties of a system from a detailed knowledge of its atomic constituents.

## J. Some important applications

### 1. Heat engines and biological systems

*a. Converting randomness into order.* The entropy of an isolated system increases as the system tends to approach a more random situation. How then can one obtain a less random situation (for example, convert the random energy of the molecules of gasoline into the nonrandom energy of forward motion of a car)?

This conversion can be done if the system  $X$  is not isolated, but interacts with its environment  $X'$ . The entropy change of the total isolated system

$$\Delta S^* = \Delta S + \Delta S' \quad (44)$$

can then be positive even if  $X$  becomes less random (so that its entropy  $S$  decreases and  $\Delta S$  is negative). This change is possible if the entropy  $S'$  of the environment increases by more than a compensating amount (that is, if the entropy change  $\Delta S'$  is positive and sufficiently large).

*b. Heat engines.* It would be very useful to have an engine that could absorb some positive heat  $q$  from a heat reservoir  $X$  at some temperature  $T$  and convert this heat into an equivalent amount of macroscopic work done on some external system. But this is impossible because the entropy of the reservoir (and thus of the entire system) would then decrease.

Suppose, however, that the engine converts only a part of the absorbed heat  $q$  into work  $w$  and rejects the remaining heat  $q' = q - w$  into some other heat reservoir  $X'$ . If the temperature  $T'$  of  $X'$  is sufficiently low, the entropy  $S'$  of  $X'$  can then increase by such a large amount that the entropy  $S^*$  of the entire system does *not* decrease.

The requirement that  $S^*$  does not decrease implies that

$$\Delta S^* = \Delta S + \Delta S' = (-q/T) + (q-w)/T' \geq 0 \quad (45)$$

or

$$w/q \leq (T - T')/T. \quad (46)$$

The fraction of work obtainable from the engine (its ‘‘efficiency’’) is, therefore, limited by the absolute temperatures of the reservoirs.<sup>29</sup>

*c. Biological systems.* Similarly, biological systems can grow (and thus become more orderly) only by increasing the randomness of their environment by more than a compensating amount. For example, an isolated kitten in a box would quickly die so that its body would decompose. However, if the box also contains food, then the kitten could grow into a cat, but the food in the kitten’s environment would be converted into excrement.

Biological processes require individual molecules to be assembled into more orderly polymers (for example, amino acids into proteins). Again this assembly can be done only by coupled chemical reactions in which other molecules (such as ATP) are transformed into more random forms.

## 2. Phase transformations

Why is it that solids change into liquids, or liquids into gases, at certain well-defined temperatures? For example, if some ice turns into water, its entropy  $S$  increases because the water molecules move about in much more random ways. However, the internal energy  $E$  of these molecules correspondingly also increases so that heat  $Q = \Delta E$  must be absorbed from the environment (which is a large heat reservoir at some temperature  $T'$ ). Hence, the energy  $E'$  of the environment must decrease by an amount  $\Delta E' = -Q$  and its entropy  $S'$  must correspondingly decrease by an amount  $\Delta S' = \Delta E'/T' = (-Q)/T'$ .

If the ice is to melt, the entropy  $S^*$  of the entire isolated system (ice and environment) must increase or remain unchanged so that

$$\Delta S^* = \Delta S + \Delta S' = \Delta S - Q/T' \geq 0. \quad (47)$$

(a) If the temperature  $T'$  is sufficiently low, melting of the ice would lead to an increase  $\Delta S$  of its entropy, but would lead to a more than compensating decrease  $\Delta S' = -Q/T'$  of the entropy of the environment. Hence it is overwhelmingly more probable that the ice remains in its frozen state. (b) At sufficiently high temperatures, the heat  $Q$  required for melting results in a much smaller entropy decrease  $\Delta S'$  of the environment. Hence the total entropy  $S^*$  is increased if the ice melts, so that this occurs with overwhelming probability.

(c) At some particular intermediate temperature, the two effects cancel so that melting results in *no* net change in the total entropy  $S^*$ . At this temperature, ice and liquid water can, therefore, coexist in equilibrium.<sup>30</sup>

## 3. Boltzmann distribution and molecular speeds

What is the probability  $P_r$  that a system  $X$  is in any *one* particular basic state  $r$ , of energy  $E_r$ , when it is in thermal contact with a large heat reservoir  $X'$  at some temperature  $T'$ ? The number of basic states available to the entire isolated system  $X^*$  (consisting of  $X$  and  $X'$ ) is the number of basic states  $\Omega'(E')$  available to the reservoir  $X'$  when its energy  $E' = E^* - E_r$  (where  $E^*$  is the constant total energy of  $X^*$ ). According to Eq. (5), the probability  $P_r$  is then

$$P_r \propto \Omega'(E^* - E_r). \quad (48)$$

If  $X$  is in a state  $r$  of higher energy, the energy  $E'$  of the reservoir (and hence the number of basic states available to it) is correspondingly smaller. Hence the probability that  $X$  is in a state of higher energy is smaller than the probability that it is in a state of lower energy.

This conclusion can be expressed quantitatively by considering the logarithm of (48) and remembering that  $E_r$  is much smaller than the total energy  $E^*$ . Thus, to lowest order,

$$\begin{aligned} \ln P_r &= \text{constant} + \sigma'(E^* - E_r) \\ &= \text{constant} + [\sigma'(E^*) - \beta' E_r], \end{aligned} \quad (49)$$

where  $\beta' = d\sigma'/dE'$  is the entropy gradient of the reservoir  $X'$ . Hence Eq. (49) implies the following result (known as the ‘‘Boltzmann distribution’’):

$$P_r \propto \exp(-\beta' E_r) \quad \text{or} \quad P_r \propto \exp(-E_r/kT'), \quad (50)$$

where  $T'$  is the absolute temperature of the reservoir.

*Application to molecular speeds in a gas.* A single molecule in a gas can be considered as a system in thermal contact with a heat reservoir consisting of all the other gas molecules and the environment of the gas (all at some absolute temperature  $T'$ ). Hence the probability  $P(\mathbf{v})$  that such a molecule, of mass  $m$ , is in a particular basic state where its digitized velocity is  $\mathbf{v}$  (and its corresponding kinetic energy is  $m v^2/2$ ) is

$$P(\mathbf{v}) \propto \exp(-m v^2/2kT'). \quad (51)$$

The probability that such a molecule has a speed in the range between  $v$  and  $v + dv$  can then be found by multiplying (51) by  $4\pi v^2 dv$  (because this factor is proportional to the number of velocities in this range).

## IV. CONCLUDING REMARKS

The preceding sections have outlined an approach whereby thermal physics can be taught from an atomistic point of view, but in a way that is sufficiently simple to be suitable for students in an introductory calculus-based physics course.

### A. Integration of microscopic and macroscopic considerations

The approach starts from the knowledge that all matter consists of atomic particles. Using some elementary ideas of mechanics and some primitive probability considerations, it

provides a seamless integration of microscopic and macroscopic considerations while preserving their distinctive virtues.

(1) The approach yields the classical laws of thermodynamics in their full generality (see Sec. III 3) and shows how these laws can be used to make purely macroscopic inferences independent of specific atomic models (for example, to infer relations between specific heats or to discuss heat engines). Furthermore, it transcends the classical laws because it also shows how the probabilities of macroscopic situations can be related to their corresponding entropies.

(2) It provides valuable physical insights about atomic mechanisms underlying observable macroscopic concepts and phenomena (such as internal energy, heat, entropy, absolute temperature, the approach to equilibrium, irreversibility, and fluctuations in equilibrium).

(3) It enables one to infer the properties of macroscopic systems from specific knowledge about their atomic constituents (for example, to predict the pressure or heat capacity of an ideal gas). It also allows one to predict the behavior of atomic particles (for example, the velocity distribution of molecules in a gas).

Hence, the suggested approach has many advantages while not omitting any significant physics ordinarily discussed from a traditional macroscopic point of view.

## B. Limitation of the approach

In its attempt to keep the discussion readily accessible to first-year college students, the approach has eschewed quantum-mechanical ideas that would not yet be familiar to such students. This limitation could easily be overcome if students already know some quantum physics, but is not of major importance in an introduction to thermal physics. Indeed, practically all the reasoning processes and results would remain unchanged in a more correct quantum-mechanical treatment. Hence the suggested approach can provide students with a very good basis for further learning after they have become familiar with quantum mechanics.

The major modifications entailed by the more correct quantum-mechanical treatment would be the following. (a) Basic states would be well-defined discrete quantum states (rather than digitized states specified by position and velocity). (b) Correspondingly, the entropy would be unambiguously defined and would approach zero when  $T \rightarrow 0$  (so that a system approaches its quantum-mechanical ground state). Thus one would also obtain the third law of thermodynamics. (c) Last, the proper quantum-mechanical description of atomic systems leads to more correct predictions of macroscopic properties (for example, of heat capacities), especially at lower absolute temperatures.

## C. Pedagogical issues

My experience indicates that the suggested approach is no more difficult (and in some respects even easier) than a largely macroscopic treatment of thermal physics. This approach can, therefore, be used to teach thermal physics in a five- or six-week period of an otherwise traditional calculus-based introductory physics course. It might also be useful to students in introductory physical chemistry courses.

The suggested atomistic approach outlined in the preceding pages can be readily expanded into more complete instructional materials (expository text and problems) suitable for the introductory physics course. Indeed, I had been

tempted to transform my own detailed instructional materials into a textbook, but did not do so because of uncertainty as to whether there would be sufficient interest to make the effort cost-effective.

## ACKNOWLEDGMENTS

I am indebted to Jill H. Larkin for many useful discussions and to Leonardo Hsu for some helpful comments.

<sup>1</sup>Electronic mail: freif+@andrew.cmu.edu

<sup>2</sup>F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965).

<sup>3</sup>F. Reif, *Statistical Physics*, Berkeley Physics Course, Vol. 5 (McGraw-Hill, New York, 1967).

<sup>4</sup>D. Halliday and R. Resnick, *Physics* (Wiley, New York, 1978), 3rd ed.

<sup>5</sup>There are, of course, other ways that thermal physics can be taught from a microscopic point of view in an introductory physics course. For example, another such recent attempt is described in T. A. Moore and D. V. Schroeder, "A different approach to introducing statistical mechanics," *Am. J. Phys.* **65**, 26–36 (1997). Also T. A. Moore, *Six Ideas That Shaped Physics (Unit T: Some Processes are Irreversible)* (McGraw-Hill, New York, 1997).

<sup>6</sup>It is wise to avoid use of the word "microscopic" because students are likely to confuse it with the similarly sounding word "macroscopic."

<sup>7</sup>Negative work done *on* the system corresponds to positive work done *by* the system. Similarly, negative heat *absorbed* by the system corresponds to positive heat given *off* by the system.

<sup>8</sup>The form (3) of the law ensures consistency with mechanics where  $W$  is used to denote the work done *on* a system. It also clearly exhibits the similarity between the work done *on* a system and the heat absorbed by it. (These advantages are not shared by a historical convention that uses  $W$  to denote the work done *by* a system.)

<sup>9</sup>The analogy is due to H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, New York, 1985), 2nd ed.

<sup>10</sup>Negative flow *into* the lake corresponds to positive flow *out* of the lake. Similarly, negative *condensation* into the lake corresponds to positive *evaporation* from the lake.

<sup>11</sup>One can check that condensation has been eliminated by also eliminating the flow and checking that the water level then remains unchanged.

<sup>12</sup>One can check that heat transfer has been eliminated by also eliminating all macroscopic work and checking that the thermometer indication then remains unchanged.

<sup>13</sup>The work  $W$  in Eq. (3) has been defined (as in mechanics) as work done *on* a system. Hence the infinitesimal work  $d'W$  done on a system by a pressure  $p$  in a small volume change  $dV$  is  $-pdV$  (that is, it is negative if the volume increases).

<sup>14</sup>All the preceding basic ideas can be illustrated by giving students some simple problems dealing with tossed coins or dice. The aim should merely be to let students exemplify the definition of probability in some very simple cases. However, there is *no* need to introduce students to more complex knowledge about probabilities.

<sup>15</sup>The term "basic state," rather than "microstate," is used here to avoid confusion with the similarly sounding word "macrostate."

<sup>16</sup>It is advisable to warn students that this specification of a basic state, although adequate for present purposes, must ultimately be replaced by a more correct quantum-mechanical specification.

<sup>17</sup>There is no need to distinguish this specification in terms of velocities from the more formal specification in terms of momenta.

<sup>18</sup>Many of today's students already know the utility of digitizing information. For example, computers use such digitizing to specify possible positions on a display by discrete positions ("pixels") or to specify possible sound intensities by discrete possible values.

<sup>19</sup>Such graphs are sufficient to show what happens when the number  $N$  of molecules becomes larger. Thus there is no real need to teach students the binomial distribution.

<sup>20</sup>Instead of observing fluctuations in an assembly of  $\mathcal{N}$  systems, one may observe a single system at a large number  $\mathcal{N}$  of successive instants (for example, by taking movie pictures every second). In a time-independent equilibrium situation the resultant pictures then constitute a statistical assembly equivalent to  $\mathcal{N}$  different systems observed at any one time. Equivalent probability statements can then be made about these pictures.

that is, about the fluctuations in a *single* system observed in the course of time.

<sup>20</sup>It is instructive to show students successive computer-generated movie frames (or actual running movies) displaying simulations of gas molecules spreading out throughout a box (or the reverse process where they concentrate themselves into one half of the box). In particular, this reverse process looks strikingly different for 40 molecules or for 4 molecules. [Such movie frames are shown on pp. 22–25 of volume 5 of the Berkeley Physics Course (see the reference in Note 2).]

<sup>21</sup>The absolute temperature can be negative if one considers special systems that have no kinetic energy. For example, as the internal energy of a system of spins in a magnetic field increases, the system's entropy first increases and then decreases. In this case  $\beta$ , as well as  $T$ , can be negative.

<sup>22</sup>Some examples or exercises with small numbers, describing unrealistically small systems, can help to clarify these considerations.

<sup>23</sup>For very simple systems, such as ideal gases, Eq. (20) is equivalent to the condition that the average energy per particle is the same in each system.

<sup>24</sup>More generally, heat flows from the system with lower  $\beta$  to the system with higher  $\beta$ . This is true even in the case of a system (of the kind mentioned in Ref. 21) where  $\beta$  or  $T$  can be negative. Unlike  $\beta$ , the absolute temperature  $T$  is then an inconvenient concept because a negative absolute temperature describes a very *warm* system whose temperature goes through infinity as the system cools down.

<sup>25</sup>The topics discussed in Sec. III G can be accompanied by many of the exercises and problems commonly used in conventional approaches to

thermal physics (for example, problems examining applications of the ideal gas laws, the temperature change caused by the free expansion of a gas, the dependence of molecular speeds on temperature or masses of the molecules, etc.).

<sup>26</sup>The notation  $d'Q$  (with a prime ornamenting the  $d$ ) is here used to denote an infinitesimal quantity which is *not* necessarily a small difference.

<sup>27</sup>It is instructive to let students contrast a *sudden* adiabatic expansion of a gas (where its entropy increases) with a *quasi-static* adiabatic expansion (where this entropy remains unchanged). It can be pointed out that the latter case involves two competing effects: (a) an increase of the entropy because of the increased gas volume and (b) a decrease of the entropy because of the decreased internal energy (caused by the negative work done on the gas during its slow expansion).

<sup>28</sup>There is no need to express these relations in terms of partial derivatives [for example, to write  $(\partial S/\partial E)_V = 1/T$ ] because beginning students may still be unfamiliar with this notation.

<sup>29</sup>Similar entropy arguments apply to refrigerators designed to transfer heat from a reservoir at a lower absolute temperature to another one at a higher temperature.

<sup>30</sup>To deal also with pressure effects, one may consider a system in contact with an environment at constant temperature  $T'$  and pressure  $p'$  so that  $\Delta S^* = \Delta S - (\Delta E + p' \Delta V)/T'$ . In this case phase transformations may again be discussed by simple entropy considerations without resorting to the Gibbs free energy.

### CHRISTMAS DINNER

At Christmas we were invited to Lawrence's home for dinner; oddly enough, he took the opportunity of telling me on this occasion that the lab was short of money, and that if necessary he would ask me to return part of my salary.

In 1939, \$300 a month was a good salary, and it got me out of the woods for some time, but after six months, in July 1939, Lawrence, who by then must have realized my situation, asked me if I could return to Palermo. I answered by telling him the truth, and he immediately interjected: "But then why should I pay you \$300 per month? From now on I will give you \$116."

Emilio Segrè, *A Mind Always in Motion—The Autobiography of Emilio Segrè* (University of California Press, Berkeley, 1993), p. 147.