A different approach to introducing statistical mechanics

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The basic notions of statistical mechanics (microstates, multiplicities) are quite simple, but understanding how the second law arises from these ideas requires working with cumbersomely large numbers. To avoid getting bogged down in mathematics, one can compute multiplicities numerically for a simple model system such as an Einstein solid—a collection of identical quantum harmonic oscillators. A computer spreadsheet program or comparable software can compute the required combinatoric functions for systems containing a few hundred oscillators and units of energy. When two such systems can exchange energy, one immediately sees that some configurations are overwhelmingly more probable than others. Graphs of entropy vs. energy for the two systems can be used to motivate the theoretical definition of temperature, $T = (\partial S/\partial U)^{-1}$, thus bridging the gap between the classical and statistical approaches to entropy. Further spreadsheet exercises can be used to compute the heat capacity of an Einstein solid, study the Boltzmann distribution, and explore the properties of a two-state paramagnetic system. ©*1997 American Association of Physics Teachers.*

I. INTRODUCTION

Entropy is a crucial concept in thermal physics. A solid understanding of what entropy is and how it works is the key to understanding a broad range of physical phenomena, and enhances one's understanding of an even wider range of phenomena. The idea of entropy and its (nearly) inevitable increase are thus core concepts that we should hope physics students at all levels would study carefully and learn to apply successfully.[1]

Unfortunately, the approach to teaching entropy found in virtually all introductory and many upper-level textbooks is more abstract than it needs to be. Such texts[2] introduce entropy in the context of macroscopic thermodynamics, using heat engines and Carnot cycles to motivate the discussion, ultimately defining entropy to be the quantity that increases by Q/T when energy Q is transferred by heating to a system at temperature T. In spite of the way that this approach mirrors the historical development of the idea of entropy, our students have usually found the intricate logic and abstraction involved in getting to this definition too subtle to give them any intuitive sense of what entropy is and what it measures; the concept ultimately remains for them simply a formula to memorize.[3] Most introductory texts attempt to deal with this problem by including a section about how entropy quantifies "disorder". The accuracy and utility of this idea, however, depends on exactly how students visualize "disorder", and in many situations this idea is unhelpful or even actively misleading.[4] The macroscopic approach therefore generally does *not* help students develop the kind of accurate and useful intuitive understanding of this very important concept that we would like them to have.

The *statistical* interpretation of entropy (as the logarithm of the the number of quantum microstates consistent with a system's macrostate) is, comparatively, quite concrete and straightforward. The problem here is that it is not trivial to show from this definition that the entropy of a macroscopic system of interacting objects will inevitably increase.[5]

This paper describes our attempt to link the statistical definition of entropy to the second law of thermodynamics in a way that is as accessible to students as possible.[6] Our primary motivation was to create a more contemporary approach to entropy to serve as the heart of one of the six modules for *Six Ideas That Shaped Physics*, a new calculus-based introductory course developed with the support and assistance of the Introductory University Physics Project (IUPP). However, we have found this approach to be equally useful in upper-level undergraduate courses.

The key to our approach is the use of a *computer* to count the numbers of microstates associated with various macrostates of a simple model system. While the processes involved in the calculation are simple and easy to understand, the computer makes it practical to do the calculation for systems large enough to display the irreversible behavior of macroscopic objects. This vividly displays the link between the statistical definition of entropy and the second law without using any sophisticated mathematics. Our approach has proved to be very helpful to upper-level students and is the basis of one of the most successful sections of the *Six Ideas* introductory course.[7] Depending on the level of the course and the time available, the computer-based approach can be used either as the primary tool or as a springboard to the more powerful analytic methods presented in statistical mechanics texts.

A number of choices are available for the specific computational environment: a standard spreadsheet program such as Microsoft *Excel* or Borland *QuattroPro*; a stand-alone program specially written for the purpose; or even a graphing calculator such as the TI-82. We will use spreadsheets in our examples in the main body of this paper, and briefly describe the other alternatives in Section VI.

After some preliminary definitions in Section II, we present the core of our approach, the consideration of two interacting "Einstein solids", in Section III. In the remaining sections we derive the relation between entropy, heat, and temperature, then go on to describe a number of other applications of spreadsheet calculations in statistical mechanics.

II. PHYSICS BACKGROUND

A. Basic Concepts of Statistical Physics

The aim of statistical mechanics is to explain the behavior of systems comprised of a very large number of particles. We can characterize the physical *state* of such a system in either of two ways, depending on whether we focus on its characteristics at the macroscopic or molecular level.

The *macrostate* of a system is its state as viewed at a macroscopic level. For instance, to describe the macrostate of a tank of helium gas, we could specify the number of molecules N it contains, the total volume V that they occupy, and their total internal energy U. As long as the gas is in internal thermal equilibrium, these three parameters suffice to determine its macrostate. (Other thermodynamic variables, such as the temperature T and the pressure P of the gas, can then be calculated using various "equations of state" such as the ideal gas law $PV = NkT$ and the relation $U = \frac{3}{2}NkT$, where k is Boltzmann's constant.) In general, the macrostate of a system is determined by the various conservation laws and physical constraints that it is subject to.

The *microstate* of a system is its state as viewed at the molecular level. To describe the microstate of our tank of helium gas, we would have to specify the exact position and velocity (or quantum mechanical wavefunction) of each individual molecule. Note that if we know a system's microstate, we also know its macrostate: The total energy U, for instance, is just the sum of the energies of all the molecules. On the other hand, knowing a system's macrostate does not mean we're anywhere close to knowing its microstate.

The number of microstates that are consistent with a given macrostate is called the *multiplicity* of that macrostate, denoted Ω. Equivalently, Ω is the number of *accessible* microstates, limited only by the constraints that determine the macrostate. For our tank of helium gas, the multiplicity would be a function of three macroscopic variables, for instance, $\Omega(U, V, N)$. In most cases the multiplicity will be a *very* large number, since there will be an enormous number of different ways to distribute a given amount of energy among the system's molecules (and, for fluids, to distribute the molecules within the available volume).

The *fundamental assumption* of statistical mechanics is that an isolated system in a given macrostate is equally likely to be in any of its accessible microstates. This means

that the probability of finding the system in any given microstate is $1/\Omega$, since there are Ω microstates, all equally probable. In the next section we will see how this assumption leads to the conclusion that macroscopic objects must exhibit *irreversible* behavior, such as the spontaneous flow of energy from a hot object to a cold one. In order to make this argument concrete, though, we will focus our attention on a specific model for a thermodynamic system, since the exact way that a macrostate's multiplicity depends on N, U, and V depends on what physical system we are considering. Once we understand how the argument works for our specific model, we will be able to understand (at least qualitatively) how it would apply to other physical systems.

B. The Einstein Solid Model

There are only a few realistic systems whose multiplicities can be calculated using elementary methods. Even an ideal gas is too complicated in this regard—a direct derivation of its multiplicity function requires some fairly sophisticated tools.[8] A much simpler system would be one whose particles are all fixed in place (so the volume is irrelevant), storing energy in units that are all the same size. This idealized model is treated in many statistical mechanics texts.[9] Physically, it corresponds to a collection of identical quantum harmonic oscillators. In 1907, Einstein proposed such a model to describe the thermal properties of a simple crystalline solid, treating each atom as an independent three-dimensional harmonic oscillator. We will therefore call this model an *Einstein solid*.

We will use N to denote the number of one-dimensional *oscillators* in an Einstein solid. (So the number of atoms is $N/3$.) If we neglect the static zero-point energy (which plays no role in the thermal behavior), then the energy of any oscillator can be written

$$E = \epsilon n, \tag{1}$$

where n is a nonnegative integer and ϵ is a constant ($\epsilon = hf$, where f is the oscillator's natural frequency). In other words, each oscillator can store any number of units of energy, all of the same size. The total energy of the entire solid can thus be written

$$U = \epsilon q, \tag{2}$$

where q is another nonnegative integer. The multiplicity of an Einstein solid is some function of N and q: the number of ways of arranging q units of energy among N oscillators.

For a very small Einstein solid one can simply *count* all the ways of arranging the energy among the oscillators. For example, if $N = q = 3$, the following 10 distinct distributions are possible (where the first number in each triplet specifies the number of energy units in the first oscillator, the second the number of energy units in the second oscillator, etc.): 300, 030, 003, 210, 120, 201, 102, 021, 012, 111. Thus the multiplicity of this macrostate is $\Omega = 10$. By directly counting microstates in this manner, one can not only vividly illustrate the concepts of macrostates and microstates to first-year students, but also show how the multiplicity increases very sharply with both N and q, without using any difficult mathematics.

The general formula for the multiplicity of an Einstein solid is

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!(N - 1)!} = \frac{(U/\epsilon + N - 1)!}{(U/\epsilon)!(N - 1)!}. \tag{3}$$

An elegant derivation of this formula can be found in the textbook of Callen.[10] In brief, the trick is to represent any microstate as a sequence of dots (representing energy units) and lines (representing partitions between one oscillator and the next). A total of q dots and $N - 1$ lines are required, for a total of $q + N - 1$ symbols. The number of possible arrangements is just the number of ways of choosing q of these symbols to be dots.

Whether or not one derives formula (3) in class, students have little trouble believing it after they have verified a few simple cases by brute-force counting. In an introductory course, this is all we usually have them do.

III. INTERACTING SYSTEMS

To understand irreversible processes and the second law, we now move on to consider a system of *two* Einstein solids, A and B, which are free to exchange energy with each other but isolated from the rest of the universe.

First we should be clear about what is meant by the "macrostate" of such a composite system. For simplicity, we assume that our two solids are *weakly coupled*, so that the exchange of energy between them is much slower than the exchange of energy among atoms within each solid. Then the individual energies of the two solids, U_A and U_B, will change only slowly; over sufficiently short time scales they are essentially fixed. We will use the word "macrostate" to refer to the state of the combined system, as specified by the (temporarily) constrained values of U_A and U_B. For any such macrostate we can compute the multiplicity, as we shall soon see. However, on longer time scales the values of U_A and U_B *will* change, so we will also talk about the *total* multiplicity of the combined system, considering all microstates to be "accessible" with only $U_{\text{total}} = U_A + U_B$ held fixed. In any case, we must also specify the number of oscillators in each solid, N_A and N_B, in order to fully describe the macrostate of the system.

Let us start with a very small system, in which each of the "solids" contains only three oscillators and the solids share a total of six units of energy:[11]

$$N_A = N_B = 3;$$
$$q_{\text{total}} = q_A + q_B = 6. \tag{4}$$

Given these parameters, we must still specify the individual value of q_A or q_B to describe the macrostate of the system. There are seven possible macrostates, with $q_A = 0, 1, \ldots 6$. For each of these macrostates, we can compute the multiplicity of the combined system as the product of the multiplicities of the individual systems:

$$\Omega_{\text{total}} = \Omega_A \Omega_B. \tag{5}$$

This works because the systems are independent of each other: For each of the Ω_A microstates accessible to solid A, there are Ω_B microstates accessible to solid B. A table of the various possible values of Ω_A, Ω_B, and Ω_{total} is shown in Fig. 1. Students can easily

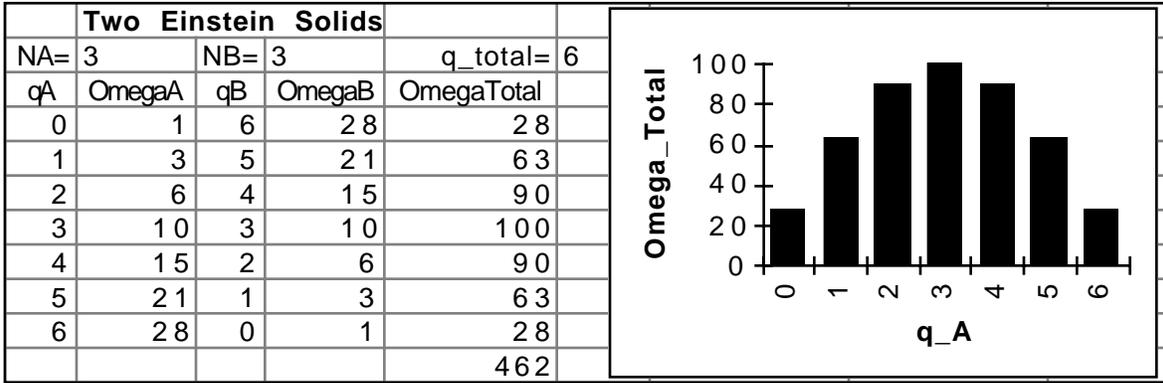| Two Einstein Solids					
NA= 3		NB= 3		q_total= 6	
qA	OmegaA	qB	OmegaB	OmegaTotal	
0	1	6	28	28	
1	3	5	21	63	
2	6	4	15	90	
3	10	3	10	100	
4	15	2	6	90	
5	21	1	3	63	
6	28	0	1	28	
				462	

Fig. 1. Computation of the multiplicies for two Einstein solids, each containing three oscillators, which share a total of six units of energy. The individual multiplicities (Ω_A and Ω_B) can be computed by simply counting the various microstates, or by applying Eq. (3). The total multiplicity Ω_{total} is the product of the individual multiplicities, because there are Ω_B microstates of solid B for *each* of the Ω_A microstates of solid A. The total number of microstates (462) is computed as the sum of the last column, but can be checked by applying Eq. (3) to the combined system of six oscillators and six energy units. The final column is plotted in the graph at right.

construct this table for themselves, computing the multiplicities by brute-force counting if necessary.

From the table we see that the fourth macrostate, in which each solid has three units of energy, has the highest multiplicity (100). Now let us invoke the fundamental assumption: On long time scales, *all* of the 462 microstates are accessible to the system, and therefore, by assumption, are equally probable. The probability of finding the system in any given *macro*state is therefore proportional to that macrostate's multiplicity. For instance, in this example the fourth macrostate is the most probable, and we would expect to find the system in this macrostate 100/462 of the time. The macrostates in which one solid or the other has all six units of energy are less probable, but not overwhelmingly so.

Another way to construct the table of Fig. 1 is to use a computer spreadsheet program. Both Microsoft *Excel* and Borland *QuattroPro* include built-in functions for computing binomial coefficients:

$$\binom{q + N - 1}{q} = \begin{cases} \texttt{COMBIN(q + N - 1, q)} & \text{in } \textit{Excel}; \\ \texttt{MULTINOMIAL(q, N - 1)} & \text{in } \textit{QuattroPro}. \end{cases} \tag{6}$$

The formulas from the *Excel* spreadsheet that produced Fig. 1 are shown in Fig. 2.

The advantage in using a computer is that it is now easy to change the parameters to consider larger systems. Changing the numbers of oscillators in the two solids can be accomplished by merely typing new numbers in cells B2 and D2. Changing the number of energy units requires also adding more lines to the spreadsheet. The spreadsheet becomes rather cumbersome with much more than a few hundred energy units, while overflow errors can occur if there are more than a few thousand oscillators in each solid. Fortunately, most of the important qualitative features of thermally interacting systems can be observed long before these limits are reached.

	A	B	C	D	E	F
1		Two Einstein Solids				
2	NA=	3	NB=	3	q_total=	6
3	qA	OmegaA	qB	OmegaB	OmegaTotal	
4	0	=COMBIN($B$2-1+A4,A4)	=$F$2-A4	=COMBIN($D$2-1+C4,C4)	=B4*D4	
5	=A4+1	=COMBIN($B$2-1+A5,A5)	=$F$2-A5	=COMBIN($D$2-1+C5,C5)	=B5*D5	
6	=A5+1	=COMBIN($B$2-1+A6,A6)	=$F$2-A6	=COMBIN($D$2-1+C6,C6)	=B6*D6	
7	=A6+1	=COMBIN($B$2-1+A7,A7)	=$F$2-A7	=COMBIN($D$2-1+C7,C7)	=B7*D7	
8	=A7+1	=COMBIN($B$2-1+A8,A8)	=$F$2-A8	=COMBIN($D$2-1+C8,C8)	=B8*D8	
9	=A8+1	=COMBIN($B$2-1+A9,A9)	=$F$2-A9	=COMBIN($D$2-1+C9,C9)	=B9*D9	
10	=A9+1	=COMBIN($B$2-1+A10,A10	=$F$2-A10	=COMBIN($D$2-1+C10,C10	=B10*D10	
11					=SUM(E4:E10	

Fig. 2. Formulas from the *Excel* spreadsheet that produced Fig. 1. (Most of the formulas can be generated automatically by copying from one row to the next. Dollar signs indicate "absolute" references, which remain unchanged when a formula is copied.)
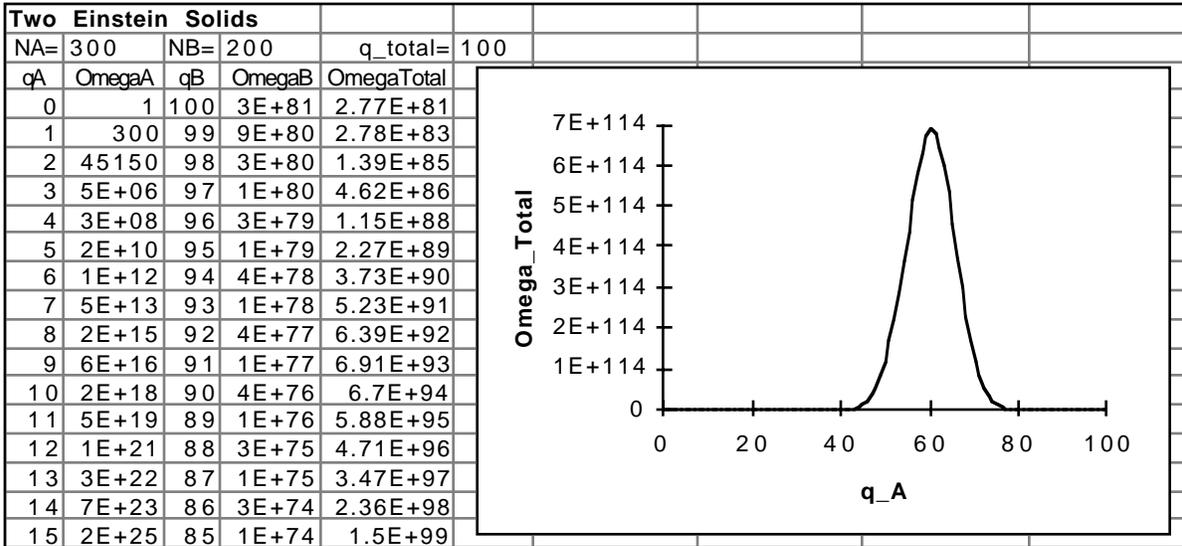

Two Einstein Solids				
NA= 300	NB= 200		q_total= 100	
qA	OmegaA	qB	OmegaB	OmegaTotal
0	1	100	3E+81	2.77E+81
1	300	99	9E+80	2.78E+83
2	45150	98	3E+80	1.39E+85
3	5E+06	97	1E+80	4.62E+86
4	3E+08	96	3E+79	1.15E+88
5	2E+10	95	1E+79	2.27E+89
6	1E+12	94	4E+78	3.73E+90
7	5E+13	93	1E+78	5.23E+91
8	2E+15	92	4E+77	6.39E+92
9	6E+16	91	1E+77	6.91E+93
10	2E+18	90	4E+76	6.7E+94
11	5E+19	89	1E+76	5.88E+95
12	1E+21	88	3E+75	4.71E+96
13	3E+22	87	1E+75	3.47E+97
14	7E+23	86	3E+74	2.36E+98
15	2E+25	85	1E+74	1.5E+99

Fig. 3. Spreadsheet calculation of the multiplicity of each macrostate, for two larger Einstein solids sharing 100 energy units. Here solids A and B contain 300 and 200 energy units, respectively. Only the first few lines of the table are shown; the table continues down to $q_A = 100$. The final column is plotted in the graph at right. Notice from the graph that the multiplicity at $q_A = 60$ is more than 10^{33} times larger than at $q_A = 0$.

Figure 3 shows a spreadsheet-generated table, and a plot of Ω_{total} vs. q_A, for the parameters

$$N_A = 300, \qquad N_B = 200, \qquad q_{\text{total}} = 100. \qquad (7)$$

We see immediately that the multiplicities are now quite large. But more importantly, the multiplicities of the various macrostates now differ by *factors* that can be very large—more than 10^{33} in the most extreme case. If we again make the fundamental assumption, this result implies that the most likely macrostates are 10^{33} times more probable than the least likely macrostates. If this system is initially in one of the less probable macrostates, and we then put the two solids in thermal contact and wait a while, we are almost *certain* to find it fairly near the most probable macrostate of $q_A = 60$ when we check again later. In other

words, this system will exhibit irreversible behavior, with net energy flowing spontaneously from one solid to the other, until it is near the most likely macrostate. This conclusion is just a statement of the second law of thermodynamics.

There is one important limitation in working with systems of only a few hundred particles. According to the graph of Fig. 3, there are actually quite a few macrostates with multiplicities nearly as large as that of the most likely macrostate. In relative terms, however, the width of this peak will decrease as the numbers of oscillators and energy units increase. This is already apparent in comparing Figs. 1 and 3. If the numbers were increased further, we would eventually find that the relative width of the peak (compared to the entire horizontal scale of the graph) is completely negligible. Unfortunately, one cannot verify this statement directly with the spreadsheets. Students in an introductory class have little trouble believing this result, when reminded of the fact that macroscopic systems contain on order of 10^{23} particles and energy units. In an upper-division course, one can prove using Stirling's approximation that the relative width of the peak is of order $1/\sqrt{N}$ or $1/\sqrt{q}$, whichever is larger. Thus, statistical fluctuations away from the most likely macrostate will be only about one part in 10^{11} for macroscopic systems.[12]

Using this result, we can state the second law more strongly: Aside from fluctuations that are normally much too small to measure, any isolated macroscopic system will inevitably evolve toward its *most* likely accessible macrostate.

Although we have proved this result only for a system of two weakly coupled Einstein solids, similar results apply to all other macroscopic systems. The details of the counting become more complex when the energy units can come in different sizes, but the essential properties of the combinatorics of large numbers do not depend on these details. If the subsystems are not weakly coupled, the division of the whole system into subsystems becomes a mere mental exercise with no real physical basis; nevertheless, the same counting arguments apply, and the system will still exhibit irreversible behavior if it is initially in a macrostate that is in some way "inhomogeneous".

IV. ENTROPY AND TEMPERATURE

Instead of always working with multiplicities, it is convenient to define the *entropy* of a system as

$$S = k \ln \Omega. \tag{8}$$

The factor of Boltzmann's constant is purely conventional, but the logarithm is important: It means that, for any given macrostate, the total entropy of two weakly interacting[13] systems is the *sum* of their individual entropies:

$$\begin{aligned} S_{\text{total}} &= k \ln(\Omega_A \Omega_B) \\ &= k \ln \Omega_A + k \ln \Omega_B \\ &= S_A + S_B. \end{aligned} \tag{9}$$

Since entropy is a strictly increasing function of multiplicity, we can restate the second law as follows: Aside from fluctuations that are normally much too small to measure, any

isolated macroscopic system will inevitably evolve toward whatever (accessible) macrostate has the largest entropy.

It is a simple matter to insert columns for S_A, S_B, and S_{total} into the spreadsheet in Fig. 3. A graph of these three quantities is shown in Fig. 4. Notice that S_{total} is *not* a strongly peaked function. Nevertheless, the analysis of the previous section tells us that, when this system is in equilibrium, it will almost certainly be found in a macrostate near $q_A = 60$.
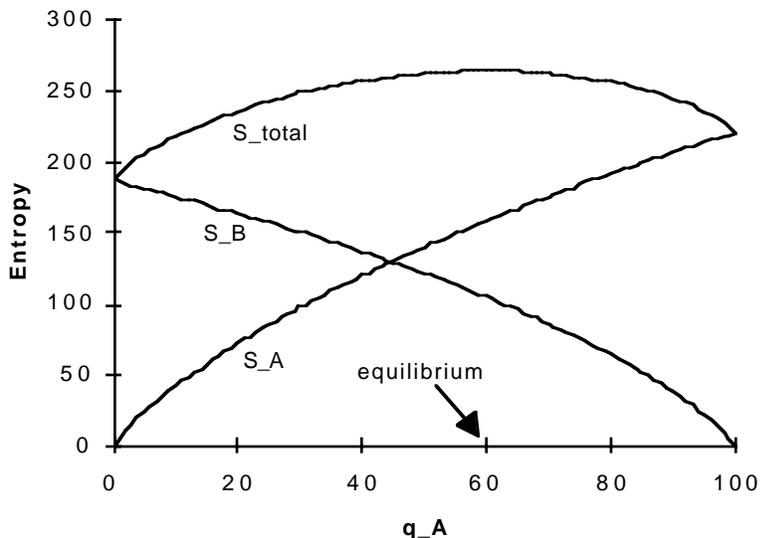

Fig. 4. A spreadsheet-generated plot of S_A, S_B, and S_{total} for the system of two Einstein solids represented in Fig. 3. At equilibrium, the slopes of the individual entropy graphs are equal in magnitude. Away from equilibrium, the solid whose slope dS/dq is *steeper* tends to gain energy, while the solid whose slope dS/dq is *shallower* tends to lose energy.

Now let us ask how entropy is related to temperature. The most fundamental way to define temperature is in terms of energy flow and thermal equilibrium: Two objects in thermal contact are said to be at the same temperature if they are in thermal equilibrium, that is, if there is no spontaneous net flow of energy between them. If energy *does* flow spontaneously from one to the other, then we say the one that loses energy has the higher temperature while the one that gains energy has the lower temperature.

Referring again to Fig. 4, it is not hard to identify a quantity that is the same for solids A and B when they are in equilibrium. Equilibrium occurs when S_{total} reaches a maximum, that is, when the slope $dS_{\text{total}}/dq_A = 0$. But this slope is the sum of the slopes of the individual entropy graphs, so their slopes must be equal in magnitude:

$$\frac{dS_A}{dq_A} = -\frac{dS_B}{dq_A} \qquad \text{at equilbrium.} \tag{10}$$

If we were to plot S_B vs. q_B instead of q_A, its slope at the equilbrium point would be equal, in sign and magnitude, to that of $S_A(q_A)$. So the quantity that is the same for both solids

when they are in equilibrium is the slope dS/dq. Temperature must be some function of this quantity.[14]

To identify the precise relation between temperature and the slope of the entropy vs. energy graph, look now to a point in Fig. 4 where q_A is larger than its equilibrium value. Here the entropy graph for solid B is steeper than that for solid A, meaning that if a bit of energy were to pass from A to B, solid B would gain more entropy than solid A loses. Since the *total* entropy would increase, the second law tells us that this process will happen spontaneously. In general, the steeper an object's entropy vs. energy graph, the more it "wants" to gain energy (in order to obey the second law), while the shallower an object's entropy vs. energy graph, the less it "minds" losing a bit of energy. We therefore conclude that temperature is *inversely* related to the slope dS/dU. In fact, the reciprocal $(dS/dU)^{-1}$ has precisely the units of temperature, so we might guess simply

$$\frac{1}{T} = \frac{dS}{dU}.$$ (11)

The factor of Boltzmann's constant in the definition (8) of entropy eliminates the need for any further constants in this formula. To confirm that this relation gives temperature in ordinary Kelvin units one must check a particular example, as we will do in the following section.

Our logical development of the concepts of entropy and temperature from statistical considerations is now complete. In the following section, we will apply these ideas to the calculation of heat capacities and other thermal properties of some simple systems. However, at this point in the development, many instructors will wish to first generalize the discussion to include systems (such as gases) whose volume can change. The derivatives in Eqs. (10) and (11) then become partial derivatives at fixed volume, and one cannot simply rearrange Eq. (11) to obtain $dS = dU/T$. There are at least two ways to get to the correct relation between entropy and temperature, and we now outline these briefly.

The standard approach in statistical mechanics texts[15] is to first consider two interacting systems separated by a movable partition, invoking the second law to identify pressure by the relation $P = T(\partial S/\partial V)_U$. Combining this relation with Eq. (11) one obtains the thermodynamic identity $dU = TdS + (-PdV)$. For quasistatic processes (in which the change in volume is sufficiently gradual), the second term is the (infinitesimal) work W done on the system.[16] But the first law says that for any process, $dU = Q + W$, where Q is the (infinitesimal) energy added by heating. Therefore, for quasistatic processes only, we can identify $TdS = Q$ or

$$dS = \frac{Q}{T} \qquad \text{(quasistatic processes only)}.$$ (12)

From this relation one can go on to treat a variety of applications, most notably engines and refrigerators.

In an introductory course, however, there may not be time for the general discussion outlined in the previous paragraph. Fortunately, if one does not need the thermodynamic

identity, some of the steps can be bypassed (at some cost in rigor). We have already seen that, when the volume of a system does not change, its entropy changes by

$$dS = \frac{dU}{T} \qquad \text{(constant volume)}. \tag{13}$$

Now consider a system whose volume does change, but that is otherwise isolated from its environment. If the change in volume is quasistatic (i.e., gradual), then the entropy of the system cannot change. Why? Theoretically, because while the energies of the system's quantum states (and of the particles in those states) will be shifted, the process is not violent enough to knock a particle from one quantum state to another; thus the multiplicity of the system remains fixed. Alternatively, we know from experiment that by reversing the direction of an adiabatic, quasistatic volume change we can return the system to a state arbitrarily close to its initial state; if its entropy had increased, this would not be possible even in the quasistatic limit. By either argument, the work done on a gas as it is compressed should not be included in the change in energy dU that contributes to the change in entropy. The natural generalization of Eq. (13) to non-constant-volume quasistatic processes is therefore to replace dU with $dU - W = Q$, the energy added to the system by heating *alone*. Thus we again arrive at Eq. (12).

V. FURTHER SPREADSHEET CALCULATIONS

So far in this paper we have used spreadsheet calculations only to gain a qualitative understanding of the second law and the relation between entropy and temperature. Now that we have developed these concepts, however, we can use the same tools to make quantitative predictions about the thermal behavior of various systems.

A. Heat Capacity of an Einstein Solid

Figure 5 shows a spreadsheet calculation of the entropy of a *single* Einstein solid of $N = 50$ oscillators with anywhere from 0 to 100 units of energy. Then, in the fourth column, we have calculated the temperature $T = \Delta U / \Delta S$ using a pair of closely spaced entropy and energy values. We have actually used a centered-difference approximation, so the cell D4, for example, contains the formula 2/(C5 − C3). Since we have omitted the constants k and ϵ from the formulas, the temperatures are expressed in units of ϵ/k.

We now know the temperature for every energy, or vice versa. In practice, however, one usually compares such predictions to experimental measurements of the *heat capacity*, defined (for systems at constant volume) as

$$C = \frac{dU}{dT} \qquad \text{(constant volume)}. \tag{14}$$

This quantity, normalized to the number of oscillators, is computed in the fifth column of the table, again using a centered-difference approximation (for instance, cell E5 contains the formula (2/(D6 − D4))/$E$1). Since we are still neglecting dimensionful constants, the entries in the column are actually for the quantity $C/(Nk)$.

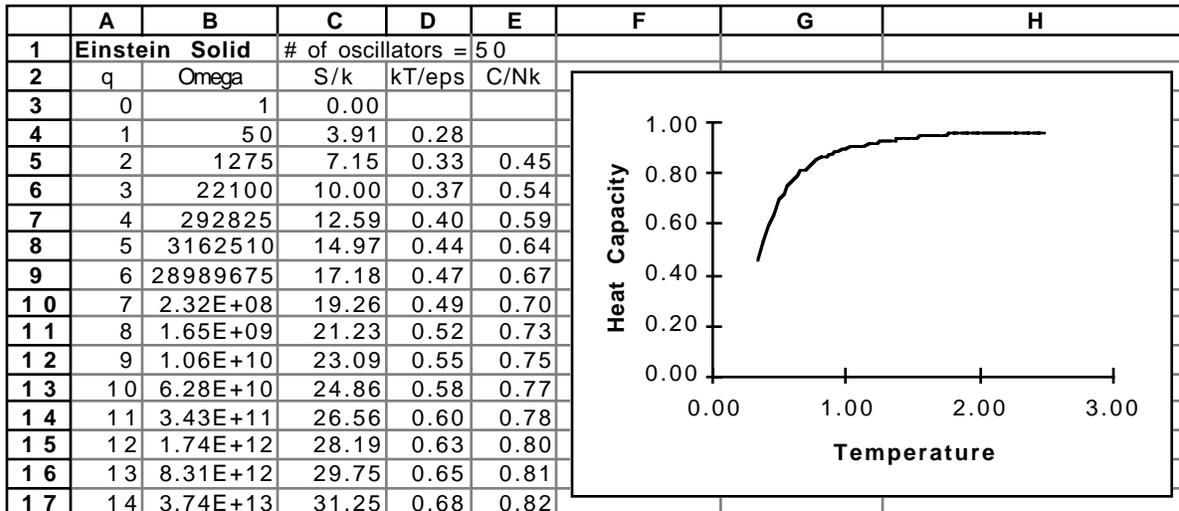|	A	B	C	D	E	F	G	H
1	Einstein Solid		# of oscillators =		50			
2	q	Omega	S/k	kT/eps	C/Nk			
3	0	1	0.00					
4	1	50	3.91	0.28				
5	2	1275	7.15	0.33	0.45			
6	3	22100	10.00	0.37	0.54			
7	4	292825	12.59	0.40	0.59			
8	5	3162510	14.97	0.44	0.64			
9	6	28989675	17.18	0.47	0.67			
10	7	2.32E+08	19.26	0.49	0.70			
11	8	1.65E+09	21.23	0.52	0.73			
12	9	1.06E+10	23.09	0.55	0.75			
13	10	6.28E+10	24.86	0.58	0.77			
14	11	3.43E+11	26.56	0.60	0.78			
15	12	1.74E+12	28.19	0.63	0.80			
16	13	8.31E+12	29.75	0.65	0.81			
17	14	3.74E+13	31.25	0.68	0.82			

Fig. 5. Spreadsheet calculation of the entropy, temperature, and heat capacity of an Einstein solid. (The table continues down to $q = 100$.) The graph at right shows the heat capacity as a function of temperature. To see the behavior at lower temperatures one can simply increase the number of oscillators in cell E1.

To the right of the table is a spreadsheet-generated graph of the heat capacity vs. temperature for this system. This theoretical prediction can now be compared to experimental data, or to the graphs often given in textbooks.[17] The quantitative agreement with experiment verifies that the formula $1/T = dS/dU$ is probably correct.[18] At high temperatures we find the constant value $C = Nk$, as expected from the equipartition theorem (with each oscillator contributing two degrees of freedom). At temperatures below ϵ/k, however, the heat capacity drops off sharply. This is just the qualitative behavior that Einstein was trying to explain with his model in 1907.

To investigate the behavior of this system at lower temperatures, one can simply increase the number of oscillators in cell E1. With 45000 oscillators the temperature goes down to about $0.1\epsilon/k$, corresponding to a heat capacity per oscillator of about $.005k$. At this point it is apparent that the curve becomes *extremely* flat at very low temperatures. Experimental measurements on real solids confirm that the heat capacity goes to zero at low temperature, but do not confirm the detailed shape of this curve. A more accurate treatment of the heat capacities of solids requires more sophisticated tools, but is given in standard textbooks.[19]

A collection of identical harmonic oscillators is actually a more accurate model of a completely different system: the vibrational degrees of freedom of an ideal diatomic gas. Here again, experiments confirm that the equipartition theorem is satisfied at high temperatures but the vibration (and its associated heat capacity) "freezes out" when $kT \ll \epsilon$. Graphs showing this behavior are included in many textbooks.[20]

B. The Boltzmann Distribution

Perhaps the most useful tool of statistical mechanics is the *Boltzmann factor*, $e^{-E/kT}$, which gives the relative probability of a system being in a microstate with energy E, when

it is in thermal contact with a much larger system (or "reservoir") at temperature T. A fairly straightforward derivation of this result can be found in most textbooks on statistical mechanics.[21] A less general derivation, based on the exponentially decreasing density of an isothermal atmosphere, is given in Serway's introductory text.[22]

Although it is no substitute for an analytic treatment, a spreadsheet calculation can easily display this exponential dependence for the case of a single one-dimensional oscillator in thermal contact with a large Einstein solid.[23] Figure 6 shows such a calculation, for the parameters $N_A = 1$, $N_B = 1000$, and $q_{\text{total}} = 100$. Here solid A is the "system", while solid B, which is much larger, is the "reservoir". The graph shows the natural logarithm of the total multiplicity, plotted as a function of q_A. According to the fundamental assumption, the total multiplicity is proportional to the probability of finding the small system in each given microstate. Note that the graph is a straight line with a negative slope: This means that the probability does indeed decay exponentially (at least approximately) as the energy $E = \epsilon q_A$ of the small system increases.

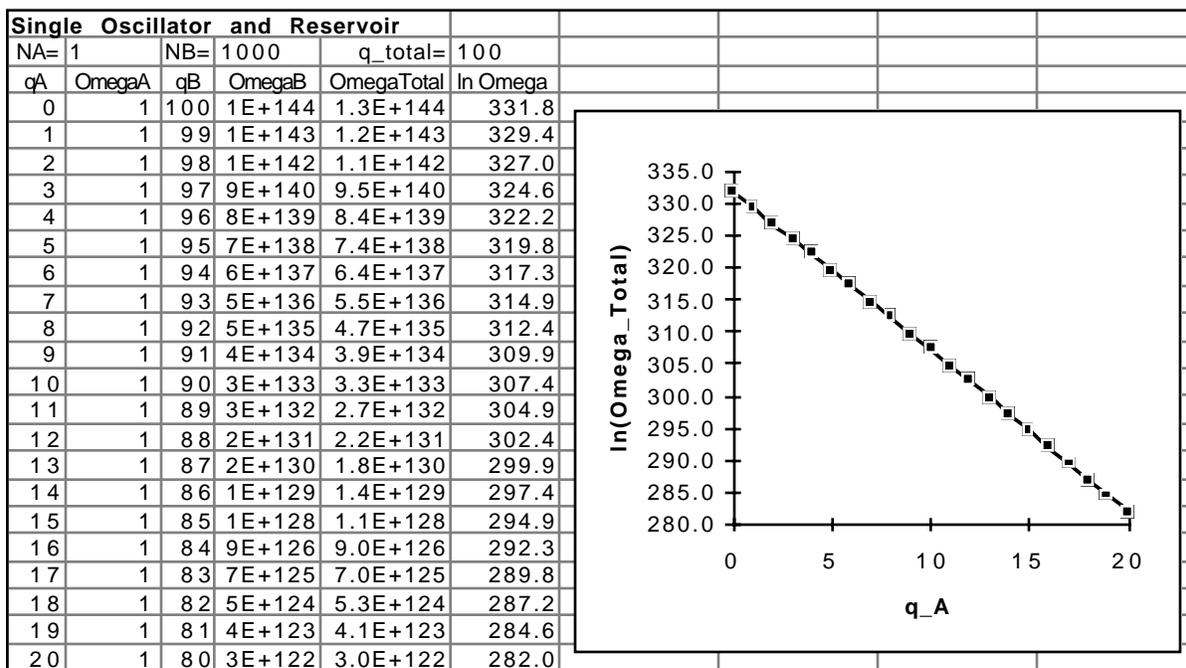| Single Oscillator and Reservoir					
NA= 1		NB= 1000		q_total= 100	
qA	OmegaA	qB	OmegaB	OmegaTotal	ln Omega
0	1	100	1E+144	1.3E+144	331.8
1	1	99	1E+143	1.2E+143	329.4
2	1	98	1E+142	1.1E+142	327.0
3	1	97	9E+140	9.5E+140	324.6
4	1	96	8E+139	8.4E+139	322.2
5	1	95	7E+138	7.4E+138	319.8
6	1	94	6E+137	6.4E+137	317.3
7	1	93	5E+136	5.5E+136	314.9
8	1	92	5E+135	4.7E+135	312.4
9	1	91	4E+134	3.9E+134	309.9
10	1	90	3E+133	3.3E+133	307.4
11	1	89	3E+132	2.7E+132	304.9
12	1	88	2E+131	2.2E+131	302.4
13	1	87	2E+130	1.8E+130	299.9
14	1	86	1E+129	1.4E+129	297.4
15	1	85	1E+128	1.1E+128	294.9
16	1	84	9E+126	9.0E+126	292.3
17	1	83	7E+125	7.0E+125	289.8
18	1	82	5E+124	5.3E+124	287.2
19	1	81	4E+123	4.1E+123	284.6
20	1	80	3E+122	3.0E+122	282.0

Fig. 6. States of a single oscillator in thermal contact with a large reservoir of identical oscillators. A graph of the logarithm of the multiplicity vs. the oscillator's energy has a constant, negative slope, in accord with the Boltzmann distribution.

According to the Boltzmann factor, the slope of the graph of multiplicity (or probability) vs. $q_A = E/\epsilon$ should equal $-\epsilon/kT$. Since the small system always has unit multiplicity and zero entropy, the entropy of the combined system is the same as the entropy of the reservoir: $S_{\text{total}} = S_B$. Once they know this, students can check either numerically or analytically that the slope of the graph is

$$\frac{\partial}{\partial q_A} \ln \Omega_{\text{total}} = \frac{\epsilon}{k} \frac{\partial S_B}{\partial U_A} = -\frac{\epsilon}{k} \frac{\partial S_B}{\partial U_B} = -\frac{\epsilon}{kT_B}, \tag{15}$$

13

where the derivatives and the temperature T_B are all evaluated at $U_A = 0$.

C. Thermal Behavior of a Two-State Paramagnet

We have used the Einstein solid model in our examples for several reasons: it is fairly realistic, its behavior is intuitive, and, most importantly, it is mathematically simple. Other systems generally lack at least one of these qualities. To carry out our spreadsheet calculations, however, all we require is mathematical simplicity.

The simplest possible system would consist of "atoms" that have only two allowed energy levels. A common example is a paramagnetic material, with one unpaired electron per atom, immersed in a uniform magnetic field B. Let us say that B points in the $+z$ direction, and quantize the spin (hence the magnetic moment) of the atom along this axis. When the magnetic moment points up, the atom is in the ground state, while when the magnetic moment points down, the atom is in the excited state. The energy levels of these two states are

$$\text{up} : E_\uparrow = -\mu B,$$
$$\text{down} : E_\downarrow = +\mu B, \tag{16}$$

where μ is the magnitude of the atom's magnetic moment. In a collection of N such atoms, the total energy will be

$$U = N_\uparrow E_\uparrow + N_\downarrow E_\downarrow = \mu B(N_\downarrow - N_\uparrow), \tag{17}$$

where $N_\uparrow$ and $N_\downarrow$ are the numbers of atoms in the up and down states. These numbers must add up to N:

$$N_\uparrow + N_\downarrow = N. \tag{18}$$

The total magnetization of the sample is given by

$$M = \mu N_\uparrow - \mu N_\downarrow = \mu(N_\uparrow - N_\downarrow) = -E/B. \tag{19}$$

To describe a macrostate of this system we would have to specify the values of N and U, or equivalently, N and $N_\uparrow$ (or N and $N_\downarrow$). The multiplicity of any such macrostate is the number of ways of choosing $N_\uparrow$ atoms from a collection of N:

$$\Omega(N, N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!(N - N_\uparrow)!} = \frac{N!}{N_\uparrow!N_\downarrow!}. \tag{20}$$

From this simple formula we can calculate the entropy, temperature, and heat capacity.

Figure 7 shows a spreadsheet calculation of these quantities for a two-state paramagnet of 100 "atoms". The rows of the table are given in order of increasing energy, which means decreasing $N_\uparrow$ and decreasing magnetization. Alongside the table is a graph of entropy vs. energy. Since the multiplicity of this system is largest when $N_\uparrow$ and $N_\downarrow$ are equal, the entropy also reaches a maximum at this point ($U = 0$) and then falls off as more energy is added. This behavior is unusual and counter-intuitive, but is a straightforward consequence of the fact that each "atom" can store only a limited amount of energy.
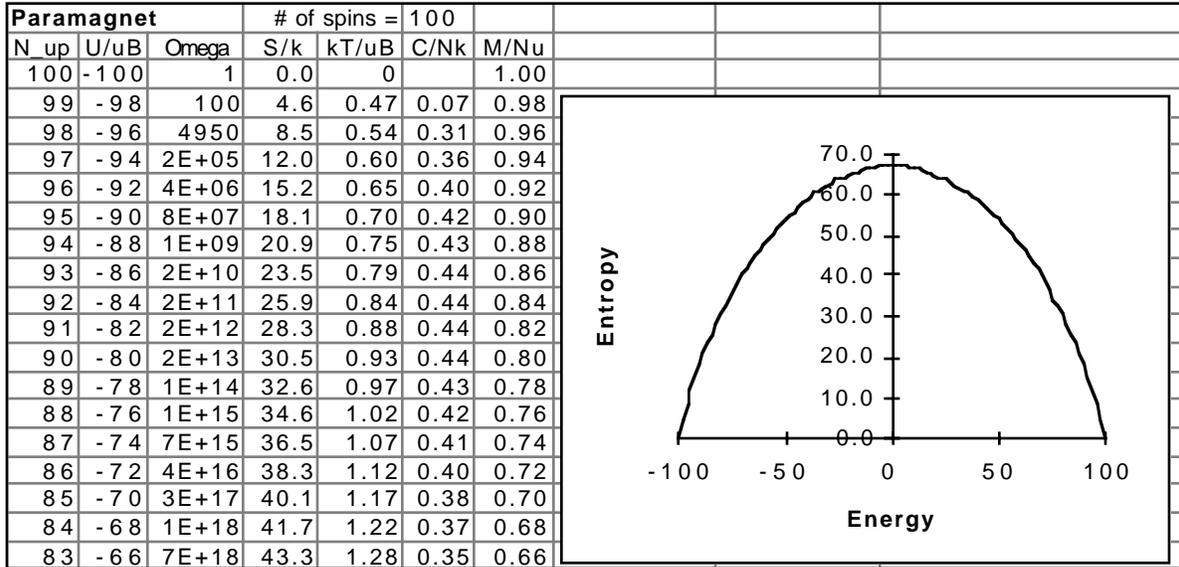
14

Paramagnet			# of spins =	100		
N_up	U/uB	Omega	S/k	kT/uB	C/Nk	M/Nu
100	-100	1	0.0	0		1.00
99	-98	100	4.6	0.47	0.07	0.98
98	-96	4950	8.5	0.54	0.31	0.96
97	-94	2E+05	12.0	0.60	0.36	0.94
96	-92	4E+06	15.2	0.65	0.40	0.92
95	-90	8E+07	18.1	0.70	0.42	0.90
94	-88	1E+09	20.9	0.75	0.43	0.88
93	-86	2E+10	23.5	0.79	0.44	0.86
92	-84	2E+11	25.9	0.84	0.44	0.84
91	-82	2E+12	28.3	0.88	0.44	0.82
90	-80	2E+13	30.5	0.93	0.44	0.80
89	-78	1E+14	32.6	0.97	0.43	0.78
88	-76	1E+15	34.6	1.02	0.42	0.76
87	-74	7E+15	36.5	1.07	0.41	0.74
86	-72	4E+16	38.3	1.12	0.40	0.72
85	-70	3E+17	40.1	1.17	0.38	0.70
84	-68	1E+18	41.7	1.22	0.37	0.68
83	-66	7E+18	43.3	1.28	0.35	0.66

Fig. 7. Spreadsheet calculation of the entropy, temperature, heat capacity, and magnetization of a two-state paramagnet. (The symbol **u** represents μ, the magnetic moment.) At right is a graph of entropy vs. energy, showing that as energy is added, the temperature (given by the reciprocal of the slope) goes to infinity and then becomes negative.

To appreciate the consequences of this behavior, imagine that the system starts out with $U < 0$ and that we gradually add more energy. At first it behaves like an Einstein solid: The slope of its entropy vs. energy graph decreases, so its tendency to suck in energy (in order to maximize its entropy in accord with the second law) decreases. In other words, the system becomes hotter. As U approaches zero, the system's desire to acquire more energy disappears. Its temperature is now infinite, meaning that it will willingly give up a bit of energy to any other system whose temperature is finite (since it loses no entropy in the process). When U increases further and becomes positive, our system actually *wants* to give up energy. Intuitively, we would say that its temperature is higher than infinity. But this is mathematical nonsense, so it is better to think about the reciprocal of the temperature, $1/T$, which is now lower than zero, in other words, negative. In these terms, our intuition even agrees with the precise relation (11).

The paramagnetic system can be an invaluable pedagogical tool, since it forces students to abandon the naive notion that temperature is merely a measure of the average energy in a system, and to embrace instead the more general relation (11), with all its connotations. One can even imagine using the paramagnet in place of the Einstein solid as the main paradigm for the lessons of Sections III and IV.[24] In particular, it is not hard to set up a spreadsheet model of two interacting paramagnets, to look at how energy can be shared between them. However, this system exhibits behavior not commonly seen in other systems or in students' prior experience. We therefore prefer not to use it as a first example, but rather to save it for an upper-level course in which students have plenty of time to retrain their intuition.

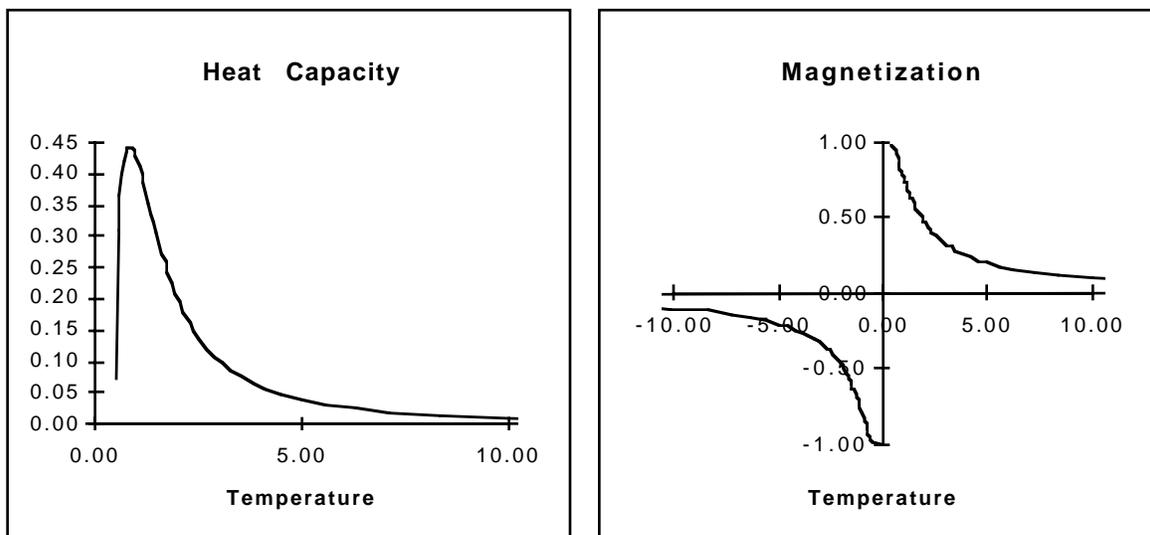Putting these fundamental issues aside, we can go on to calculate both the heat capacity

Fig. 8. Graphs of the heat capacity and magnetization as a function of temperature for a two-state paramagnet, generated from the last three columns of the spreadsheet shown in Fig. 7.

and the magnetization of our two-state paramagnet as a function of temperature. Plots of these quantities are shown in Fig. 8. Since the heat capacity goes to zero at high temperature, the equipartition theorem fails utterly to describe this system (as it must, since it applies only to degrees of freedom for which the energy is a quadratic function of a coordinate or momentum). The magnetization is complete at T just greater than zero, but drops off as the temperature is increased. The behavior in the high-temperature limit is known as Curie's law, as described in many textbooks.[25]

VI. IMPLEMENTATION DETAILS

The ideas presented in this paper have been tested, in various forms, in calculus-based introductory courses at Pomona College, Grinnell College, Smith College, Amherst College, and St. Lawrence University, and in an upper-division thermodynamics course at Weber State University. We have found that students at either level are quite able to understand the fundamental concepts of statistical mechanics that we are trying to teach. In particular, the fact that the statistical approach to the second law is more "modern" does not, in our opinion, make it unsuitable for first-year students. On the contrary, we have had far more success in teaching the statistical approach than in teaching the concept of entropy from the older classical viewpoint used in most texts.

The use of computers in our approach does not seem to pose a barrier to today's students. Many of them have had previous experience with spreadsheet programs, and the rest are able to learn very quickly with the help of a one-page instruction sheet that we have prepared.[26]

A. Sample Exercises

We generally present all of the material of Section III in class, and hand out reproductions of the figures from that section. For homework, we ask students to reproduce Fig. 1, then change the parameters to look at some larger systems. Here is a typical homework assignment, written for students who will be using *Excel*:

1. List all the possible microstates for an Einstein solid containing three oscillators and five units of energy. Verify that $\Omega = \binom{5+3-1}{5}$.

2. Set up an *Excel* spreadsheet identical (initially) to the one shown on the handouts: two Einstein solids, each containing three harmonic oscillators, with a total of six units of energy. You'll need to type in all the labels and formulas down to row 4, as well as cell A5. After that, you can use the "Fill Down" command to fill in the rest (except for cell E11). Use the "chart wizard tool" (the second icon from the right) to create the graph. Check that your spreadsheet yields all the same results as on the handout. Then modify your spreadsheet to show the case where one Einstein solid contains six harmonic oscillators and the other contains four harmonic oscillators (with the total number of energy units still equal to six). Turn in a printout of the modified spreadsheet. Assuming that all microstates are equally likely, what is the most probable macrostate, and what is its probability? What is the least probable macrostate, and what is its probability?

3. Modify your spreadsheet from the previous problem to show the case where solid A contains 100 oscillators, solid B contains 200 oscillators, and there are 100 units of energy in total. It's easiest to delete the old graph and make a new one, and this time it's best to make it an "XY (scatter)" graph instead of a column graph. Turn in a printout of the first several rows of the spreadsheet as well as the graph. What is the most probable macrostate, and what is its probability? What is the least probable macrostate, and what is its probability? Calculate the entropies of these two macrostates (expressed as unitless numbers, neglecting the factor of Boltzmann's constant).

4. Starting with your spreadsheet from the previous problem, add columns for the entropy of solid A, the entropy of solid B, and the total entropy. Print a graph showing all three entropies, plotted vs. the energy of solid A. Use the formula $T = \Delta U/\Delta S$ to calculate the temperatures of both solids (in units of ϵ/k) at the equilbrium point and also at the point $q_A = 60$. Do your results make sense? Explain.

We have also given computer-based homework assignments on the material of Section V. In upper-division courses we have asked students to generate Fig. 5 before seeing it in class. The treatment of this material can vary greatly depending on how the class is taught, however, so we will not reproduce our homework exercises here.

B. Alternative Computational Environments

Spreadsheet programs provide an almost ideal computational environment for the calculations described in this paper: they are versatile, easy to learn, and readily available on most campuses. Other computing options may be more suitable in some contexts, however.

Before we discovered spreadsheets, one of us (T. A. M.) wrote a stand-alone program for the Macintosh to produce tables and graphs such as those shown in Figs. 1 and 3. The stand-alone program is even easier to use than a spreadsheet, and can conveniently handle somewhat larger systems and values of q. It also allows one to completely omit formula (3) from the course if desired—students can simply be asked to verify the computer's computations in a few simple cases. This program is sufficient to teach the core of our approach, as outlined in Section III. A copy of the program is available on request.[27]

A much cheaper, but less convenient, option is to perform the calculations on a modern graphing calculator. We do not particularly recommend this; in our experience, graphing calculators are *much* harder to use than spreadsheet programs. However, a motivated student who already knows how to use the calculator should be able to reproduce all the major results in this paper without too much difficulty. As an example, we describe here an appropriate set of instructions for the TI-82.[28]

To set up tables like those shown in Section III, one can use the "table" feature of the TI-82, which displays seven rows at a time, calculating each row as it is displayed. The first column of the table, labeled X, should be used for q_A. The following formulas in the "Y=" screen will then generate the remaining four columns:

$$Y_1 = (X + A - 1) \text{ nCr } X$$
$$Y_2 = Q - X$$
$$Y_3 = (Y_2 + B - 1) \text{ nCr } Y_2$$
$$Y_4 = Y_1 * Y_3$$

Here we are using variables A, B, and Q to hold the constants N_A, N_B, and q_{total}, respectively. Before plotting a graph, it is best to set Xmin to zero and Xmax to 94; this insures that each pixel corresponds to an integer value of X.

To calculate temperatures and heat capacities on the TI-82, one must use "lists" instead of "tables". The following sequence of instructions will reproduce most of Fig. 5, storing q, Ω, S/k, kT/ϵ, and C/Nk in lists L_1 through L_5:

$$\text{seq}(X, X, 0, 50, 1) \rightarrow L_1$$
$$\text{seq}((X + A - 1) \text{ nCrX}, X, 0, 50, 1) \rightarrow L_2$$
$$\ln(L_2) \rightarrow L_3$$
$$\text{seq}(2/(L_3(X + 2) - L_3(X)), X, 1, 49, 1) \rightarrow L_4$$
$$\text{seq}(2/(L_4(X + 2) - L_4(X))/A, X, 1, 47, 1) \rightarrow L_5$$

Again we assume that the number of oscillators is stored in variable A. Lists 4 and 5 will be offset upward by one and two places respectively, but this can be fixed by entering "stat-edit" mode and inserting zeros. One should also add zeros at the end to make all lists the same length. It is then a simple matter to plot the heat capacity vs. the temperature, as shown in Fig. 5. Unfortunately, the lists will not update automatically when the value of A is changed.

Notes

[1]An overview of various ways of thinking about entropy has been given by Keith Andrew, "Entropy," Am. J. Phys. **52**(6), 492–496 (1984).

[2]For instance, David Halliday, Robert Resnick, and Jearl Walker, *Fundamentals of Physics* (Wiley, New York, 1993), 4th ed.; Raymond A. Serway, *Physics for Scientists and Engineers* (Saunders College Publishing, Philadelphia, 1996), 4th ed.; Francis W. Sears and Gerhard L. Salinger, *Thermodynamics, Kinetic Theory, and Statistical Thermodynamics* (Addison-Wesley, Reading, MA, 1975), 3rd ed.

[3]Rudolf Clausius himself remarked that "the second law of thermodynamics is much harder for the mind to grasp than the first," as quoted in Abraham Pais, *Subtle is the Lord* (Oxford University Press, Oxford, 1982), p. 60.

[4]For example, a deep understanding of entropy and the behavior of self-organizing systems makes it clear that biological life is fully consistent with (and is indeed an expression of) the increase of entropy, even though life apparently involves an *increase* of order in the universe. Similarly, it is not obvious that a disorderly pile of ice chips has less entropy than a simple and seemingly orderly cup of the same amount of water.

[5]Boltzmann himself had a great deal of trouble convincing the scientific community of the validity of this statistical approach to entropy. See Pais, *op. cit.*, pp. 60–68, 82–83. Arthur Beiser comments on page 315 in his *Concepts of Modern Physics* text (4th ed., McGraw-Hill, New York, 1987) that "battles with nonbelievers left him severely depressed" and contributed to his eventual suicide in 1906, just as experimental evidence in favor of the atomic hypothesis and Boltzmann's approach to thermal physics began to become overwhelming.

[6]For another attempt to address the same issue, see Ralph Baierlein, "Entropy and the second law: A pedagogical alternative," Am. J. Phys. **62**(1), 15–26 (1994). Baierlein's approach is less quantitative than ours, but full of physical insight.

[7]A complete text for a three-week introductory-level unit on thermal physics based on this approach is available. Please contact Thomas Moore for more information.

[8]A partial derivation can be found in Keith Stowe, *Introduction to Statistical Mechanics and Thermodynamics* (Wiley, New York, 1984), pp. 191–192. A very nice indirect approach to the multiplicity of an ideal gas has been given by David K. Nartonis, "Using the ideal gas to illustrate the connection between the Clausius and Boltzmann definitions of entropy," Am. J. Phys. **44**(10), 1008–1009 (1976).

[9]See, for example, Henry A. Bent, *The Second Law* (Oxford University Press, New York, 1965), pp. 144–162; Herbert B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, New York, 1985), 2nd ed., p. 334; W. G. V. Rosser, *An Introduction to Statistical Physics* (Ellis Horwood Limited, Chichester, 1982), pp. 31–41; Charles A. Whitney, *Random Processes in Physical Systems* (Wiley, New York, 1990), pp. 97–139. An even simpler model is a two-state system, as treated, for example, in Charles Kittel and Herbert Kroemer, *Thermal Physics* (Freeman, San Francisco, 1980), 2nd ed., pp. 10–21.

We treat this model in Section V.C below, and also discuss there why we don't use it as our primary example.

[10] Callen, *op. cit.*, p. 334.

[11] This same example has been used independently by Whitney, *op. cit.*, p. 126. We are grateful to one of our reviewers for pointing out this reference to us.

[12] A nice calculation of the width of the peak for a simpler system has been given by Ralph Baierlein, "Teaching the approach to thermodynamic equilibrium: Some pictures that help," Am. J. Phys. **46**(10), 1042–1045 (1978).

[13] The definition of entropy, like that of macrostate or multiplicity, depends on the time scale under consideration. Here we are interested in time scales that are long compared to the relaxation time of each individual system, but short compared to the relaxation time of the composite system. For a strongly coupled system this clean separation of time scales would not be possible. Note that on very long time scales, even our weakly coupled system would have a slightly larger entropy, equal to $k \ln \Omega$ where Ω is the total multiplicity for *all* allowed values of U_A and U_B. For macroscopic systems this number is practically indistinguishable from the quantity $k \ln(\Omega_A \Omega_B)$ computed for the most likely macrostate. A careful discussion of the role of time scales in defining entropy is given in L. D. Landau and E. M. Lifshitz, *Statistical Physics*, tr. J. B. Sykes and M. J. Kearsley (Pergamon, Oxford, 1980), 3rd edition, Part 1, p. 27.

[14] Notice that the preceding argument depends crucially on the additivity of $S = k \ln \Omega$ for the composite system. Thus the logarithm in the definition of S is essential, if S and T are to be related in a simple way.

[15] For instance, F. Mandl, *Statistical Physics* (Wiley, Chichester, 1988), 2nd ed., pp. 47, 83–87.

[16] The standard notation is $đW$, but it is too tempting to read this incorrectly as the "change in work" (a meaningless phrase), rather than correctly as an infinitesimal "amount of work". We therefore call it simply W, with the understanding that in this context it is an infinitesimal quantity. Similarly, we use Q instead of $đQ$. Note also that we take W to be positive when work is done *on* the system.

[17] See, for instance, Halliday, Resnick, and Walker, *op. cit.*, Fig. 20-2.

[18] Most textbooks define the temperature scale operationally in terms of a gas thermometer. The most direct verification of $1/T = dS/dU$ would therefore be to apply this formula directly to an ideal gas. But the gas thermometer can be used to measure the heat capacity of a solid, and this result, in turn, can be compared to our theoretical prediction. Note, in particular, that the factor of Boltzmann's constant in the definition of S conveniently makes the temperature come out in ordinary Kelvin units, with no further constants needed.

[19] For instance, Mandl, *op. cit.*, chapter 6.

[20] For instance, Halliday, Resnick, and Walker, *op. cit.*, Fig. 21-13.

[21] For instance, Callen, *op. cit.*, p. 350; Mandl, *op. cit.*, pp. 52–56; Stowe, *op. cit.*, pp. 284–287.

[22]Serway, *op. cit.*, pp. 599–601.

[23]Similar calculations can be done by hand, albeit for a somewhat smaller "large" system. See Whitney, *op. cit.*, p. 128.

[24]The two-state model system is used to introduce statistical concepts in the popular text of Kittel and Kroemer, *op. cit.*. This text includes a nice calculation of the sharpness of the multiplicity function for a system of two interacting paramagnets.

[25]Halliday, Resnick, and Walker, *op. cit.*, p. 928.

[26]This instruction sheet, which is written for users of *Excel* on the Macintosh, is available on request from Daniel Schroeder.

[27]Please send requests to Thomas Moore. Note that the program runs only on the Macintosh; no version for DOS or Windows is available.

[28]Since the TI-82 overflows at 10^{100}, one is limited to somewhat smaller systems than we have used in our earlier examples. In practice this is not much of a limitation.