

# Macrostates and Microstates

## T4

### Chapter Overview

#### Introduction

The ideal gas model we explored in chapters T2 and T3 is useful in many ways, but it does not really help us understand why some processes are irreversible. We will discuss this problem in the next three chapters. This particular chapter introduces the crucial concept of *multiplicity* and develops a model for a monatomic solid that we will use throughout the discussion.

#### Section T4.1: Distinguishing Macrostates from Microstates

We describe a system's macrostate by listing its macroscopic properties, but its microstate by specifying the quantum state of every molecule in the system. In principle we can calculate a system's macroscopic properties (and thus its macrostate), knowing its microstate. In general, there are an immense number of microstates corresponding to any given macrostate; for example, we can distribute energy in many ways among an object's atoms without affecting its macroscopic total energy  $U$ .

#### Section T4.2: The Einstein Model of a Solid

We can model a monatomic solid by imagining that each of its atoms independently oscillates around its equilibrium position. Mathematically, we can treat an atom's oscillation in three dimensions as three independent one-dimensional oscillations, one along each coordinate axis. Since the atoms are identical and the coordinate axes equivalent, we can model an  $N$ -atom solid as being  $3N$  identical but independent one-dimensional quantum oscillators. We call a solid that is adequately described by this simple model an **Einstein solid**.

According to unit Q, a one-dimensional quantum oscillator has evenly spaced energy levels separated by  $\epsilon \equiv \hbar(k_s/m)^{1/2}$ , where  $k_s$  is the effective spring constant of the interactions holding an atom to its equilibrium position,  $m$  is the atom's mass, and  $\hbar$  is Planck's constant over  $2\pi$ . If we define our zero of energy so that the oscillator's ground state corresponds to zero energy, then the energy of any one of our  $3N$  oscillators is simply an integer multiple of  $\epsilon$ . An Einstein solid's total thermal energy is therefore

$$U = \sum_{i=1}^{3N} \epsilon n_i \quad (\text{T4.5})$$

**Purpose:** This equation specifies an Einstein solid's total thermal energy  $U$ .  
**Symbols:**  $n_1, n_2, n_3, \dots$  are a set of nonnegative integers (three per atom), and  $\epsilon$  is the fixed difference between energy levels of each oscillator.  
**Limitations:** The Einstein model only works well for monatomic solids at temperatures above 100 K or so (the exact limit depends on the solid).

► Fundamentals of Thermal Physics

△ The Meaning of Entropy

Macrostates and Microstates

← The Second Law

Temperature and Entropy

► Implications and Applications

### Section T4.3: Counting Microstates

If we assume that an Einstein solid's volume is fixed, its macrostate is adequately described by its total thermal energy  $U$  and the number of atoms  $N$ . The multiplicity  $\Omega$  of such a macrostate is therefore simply the number of different ways we can add  $3N$  integer multiples of  $\epsilon$  to get  $U$ . The general formula (see problem T4S.8) turns out to be

$$\Omega(N, U) = \frac{(q + 3N - 1)!}{q!(3N - 1)!} \quad (\text{T4.6})$$

**Purpose:** This equation specifies the multiplicity  $\Omega$  of an Einstein solid's macrostate.

**Symbols:**  $N$  is the number of atoms in the solid,  $U$  is its total energy,  $q \equiv U/\epsilon$  is the number of energy units to be distributed among the atoms,  $n!$  or  $n$  factorial  $\equiv 1 \cdot 2 \cdot 3 \cdots (n - 1) \cdot n$ .

**Limitations:** This equation only applies to an Einstein solid.

### Section T4.4: Two Einstein Solids in Thermal Contact

Imagine now that we bring two Einstein solids  $A$  and  $B$  into thermal contact but isolate them from everything else (so that the combined system's total energy is fixed). We describe a macropartition of the combined system by specifying the macrostate of each solid. A macropartition table lists all the combined system's macropartitions and their multiplicities. Table T4.1 is a macropartition table for the case where  $N_A = N_B = 1$  and the combined system's total energy is  $U = U_A + U_B = 6\epsilon$ .

Note that the combined system's multiplicity  $\Omega_{AB}$  in a given macropartition is

the product of the multiplicities of each subsystem, because for each one of the  $\Omega_A$  possible microstates for solid  $A$ , there are  $\Omega_B$  possible microstates for solid  $B$  consistent with the macropartition.

### Section T4.5: The Fundamental Assumption

The fundamental assumption of statistical mechanics is that all a system's accessible microstates are equally likely in the long run. This means that as the solids randomly exchange energy, a macropartition embracing many microstates is more probable than one embracing only a few. Thus we are likely to see the 3:3 macropartition in table T4.1 about  $100/28 = 3.6$  times more often than either the 0:6 or 6:0 macropartitions.

### Section T4.6: Using StatMech

Creating tables by hand for systems having more than a handful of atoms and/or energy units becomes very tedious, but a computer can do the necessary calculations rapidly and accurately. The program StatMech (which you can download from the *Six Ideas* website) constructs such tables for larger systems.

**Table T4.1** Possible macropartitions for  $N_A = N_B = 1$ ,  $U = 6\epsilon$

Macropartition	$U_A$	$U_B$	$\Omega_A$	$\Omega_B$	$\Omega_{AB}$
0:6	0	6	1	28	28
1:5	1	5	3	21	63
2:4	2	4	6	15	90
3:3	3	3	10	10	100
4:2	4	2	15	6	90
5:1	5	1	21	3	63
6:0	6	0	28	1	28
Grand total number of microstates = 462					



## T4.1 Distinguishing Macrostates from Microstates

In this chapter, we begin exploring Boltzmann's solution to the puzzle of irreversibility. The first step in understanding this solution is to understand the crucial distinction between the *macrostate* and the *microstate* of a thermodynamic system.

### Definition of macrostate

The **macrostate** of a thermodynamic system is that system's state as characterized by its *macroscopically measurable properties*. We say, for example, that a system has the same macrostate at two different instants of time if and only if *all* its macroscopically measurable properties are the same at those two instants. We can completely describe a system's macrostate by specifying some minimal set of macroscopic properties that suffice to calculate all its other properties. For example, we saw in chapter T3 that we can completely describe an ideal gas's macrostate by specifying its chemical composition and values for its thermal energy  $U$ , its volume  $V$ , and the number of molecules  $N$ . A system's **microstate**, on the other hand, is characterized by describing the state of *each individual molecule* in the system at a given time. In the context of newtonian mechanics, we might characterize a structureless particle's state by describing its position  $[x, y, z]$  and velocity  $[v_x, v_y, v_z]$ : if we know these six quantities (as well as the molecular mass  $m$ ), we could calculate any other quantity of interest for the particle (such as its kinetic energy, its potential energy relative to any other particle, and so on). So to specify the newtonian macrostate of a monatomic system containing  $N$  identical atoms, we have to specify a minimum of  $6N$  numbers. Note that while this idea is *conceptually* straightforward, there are so many atoms in even the tiniest speck of substance that it would be impossible in *practice* to measure these numbers at a given time. (Even simply writing them down would require more time than the projected lifetime of the sun.)

### Definition of microstate

Actually, it is better to describe the state of something as small as a molecule using *quantum* mechanics instead of newtonian mechanics. In quantum mechanics, we describe the state of a given quantum in a system by specifying the quantum's energy level in the context of a certain model of the system. For example, we might model a molecule in a monatomic ideal gas as being a "quantum in a box" (in the language of unit  $Q$ ), where the "box" is the container holding the gas. As we saw in unit Q, we can specify the energy state of a quantum moving in a *one-dimensional* box by a single integer  $n$  specifying how many half-wavelengths of the quantum's wave function fit between the box boundaries. To describe a quantum's quantum state in a *three-dimensional* box, we need to specify *three* integers  $n_x, n_y$ , and  $n_z$  (which describe how many half-wavelengths of the quantum's wave function fit between the box walls along the  $x, y$ , and  $z$  axes, respectively). So to describe the microstate of an ideal monatomic gas according to the box model, we need to list  $3N$  numbers, three for every atom.

Note that if we know the microstate of a given thermodynamic system, we know its macroscopic properties as well. For example, imagine we have a sample of a monatomic ideal gas whose molecules have mass  $m$ , and we are given a list of the newtonian positions and velocities of all its molecules. By counting the numbers in the list, we can determine  $N$ , and the volume of the smallest box enclosing all the molecular positions gives us  $V$ . We can also calculate the kinetic energy of each molecule, and then add the results to find the total thermal energy  $U$  of the gas. This is enough information to specify the sample's macrostate.

The most important thing to understand about microstates and macrostates is that a system in a given, well-specified macrostate could be in any

There are *many* microstates in a macrostate



one of a *huge* number of different microstates that we are unable to distinguish by macroscopic measurements. For example, imagine we describe the macrostate of an ideal monatomic gas by stating values for  $U$ ,  $V$ , and  $N$ . There are a myriad of possible microstates that nonetheless add up to the same total  $U$  (each simply corresponds to a different way of distributing that total energy among the molecules). For any complex system, there are an immense number of possible microstates consistent with any given macrostate.

Perhaps the following analogy will make these ideas more vivid. Consider your room. It has two fundamental "macrostates" that a person (say, your parent) can rapidly discern without much detailed examination: "clean" or "messy." Describing your room's microstate, on the other hand, would involve meticulous documentation of the exact position and orientation of every object in the room. Now, there are probably a fairly large number of arrangements of objects in your room that your parent might consider clean (e.g., there are a number of possible ways to arrange your socks in the dresser drawer). There are vastly more possibilities for object arrangements that your parent would consider messy (just imagine the number of ways you could distribute your socks on the floor!). Either way, though, there are many microstates in a macrostate.

## T4.2 The Einstein Model of a Solid

To actually *count* how many microstates there are in a macrostate, we need to talk about a specific model of a system. For the remainder of this chapter (and chapter T5), I will focus on a particular simplified model for a monatomic solid.

In 1907, Albert Einstein published a paper that proposed a simple but reasonably accurate model for predicting the thermal behavior of monatomic solids (such as crystals of pure aluminum, copper, carbon, or gold). Einstein proposed treating the atoms in such a solid as if they were held in their lattice position by springs, as illustrated in figure T4.1. In a real solid, the atoms are actually held in place by interatomic electromagnetic interactions. However, as we saw in unit C, the potential energy functions for such interactions become approximately the same as those for a mass on a spring in the small-oscillation limit. So in this model, we will assume that each atom's potential energy when it is a distance  $r$  from its equilibrium position is  $\frac{1}{2}k_s r^2$  independent of the direction of  $r$ , just as it would be if it were connected to its equilibrium position by an ideal spring whose spring constant is  $k_s$ .

In both newtonian and quantum mechanics, we can treat a particle oscillating in three dimensions as if it were three independent *one-dimensional* oscillators. For example, the total newtonian energy of a three-dimensional harmonic oscillator is

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}k_s r^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) + \frac{1}{2}k_s(x^2 + y^2 + z^2) \quad (\text{T4.1})$$

where  $m$  is the atom's mass. Note how the terms in the energy equation can be grouped into three pairs, each pair of which would be the energy associated with a *one-dimensional* oscillation along one of the coordinate axes, without any reference to what is happening in the other coordinate directions. One can also show from this equation (see problem T4A.1) that the

We can treat a three-dimensional oscillator as three one-dimensional oscillators

The model treats atoms as independent oscillators



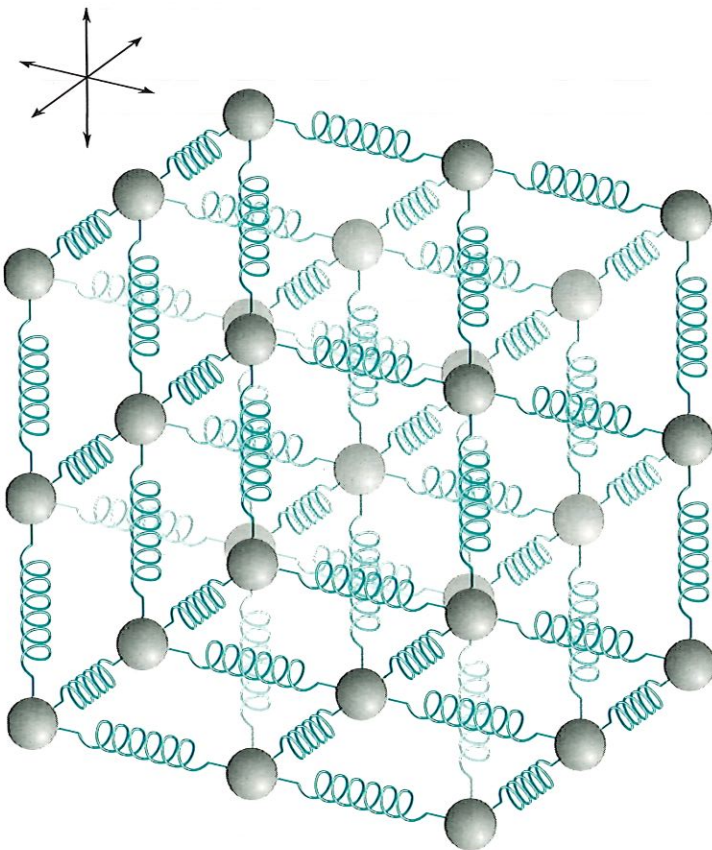


Figure T4.1

In Einstein's model of a monatomic crystalline solid, we imagine the atoms to be held in their positions by springs.

atom's motion along each coordinate axis is exactly as if the atom were oscillating in one dimension along that axis alone. (This is a special property of the harmonic oscillator potential energy function; most other potential energy functions cannot be pulled apart in this way.)

According to quantum mechanics, the energy associated with each of these separate one-dimensional oscillations is quantized, so that the atom's total vibrational energy is given by

$$(T4.2) \quad E = h\omega(n_x + \frac{1}{2}) + h\omega(n_y + \frac{1}{2}) + h\omega(n_z + \frac{1}{2})$$

where  $\omega = (k_s/m)^{1/2}$  is the angular frequency of the equivalent newtonian oscillator and  $h \equiv h/2\pi$  where  $h$  is Planck's constant. The quantities  $n_x$ ,  $n_y$ , and  $n_z$  here are independent, nonnegative integers (0, 1, 2, 3, and so on) that specify each oscillator's energy level. Each of the three terms here is the same as the expression for the energy of a one-dimensional quantum harmonic oscillator (as we saw in unit Q).

We can rewrite this equation as

$$(T4.3) \quad E = \sum_{i=1}^3 h\omega(n_i + \frac{1}{2}) = \sum_{i=1}^3 \varepsilon(n_i + \frac{1}{2})$$

where  $\varepsilon \equiv h\omega$  is the energy difference between adjacent levels of each one-dimensional oscillator and  $n_1$ ,  $n_2$ , and  $n_3$  are just a different way of labeling



the integers  $n_x$ ,  $n_y$ , and  $n_z$ . We can then find the solid's total energy by summing this over all atoms (three terms per atom):

$$E_{\text{tot}} = \sum_{3N} \epsilon \left( n_i + \frac{1}{2} \right) = \sum_{3N} \epsilon n_i + \sum_{3N} \frac{1}{2} \epsilon = \sum_{3N} \epsilon n_i + \frac{1}{2} N \epsilon \quad (\text{T4.4})$$

Now, the constant  $(3/2)N\epsilon$  term in this equation is called the solid's

**zero-point energy.** The solid will have this energy at absolute zero (which is the temperature where all atoms are in their *lowest possible* energy state, by definition). We usually define a system's *thermal* energy  $U$  in a given macrostate to be the difference between its energy in that state and the energy it would have at  $T = 0$ , so that  $U$  expresses the part of the system's energy that can *change* in thermodynamic processes. Therefore, we do not consider zero-point energy to be part of the solid's *thermal* energy  $U$ . So

$$U = \sum_{3N} \epsilon n_i \quad (\text{T4.5})$$

**Purpose:** This equation specifies the total thermal energy  $U$  of an Einstein solid whose  $N$  atoms we model as  $3N$  identical but independent quantum harmonic oscillators.

**Symbols:**  $n_1, n_2, n_3, \dots$  are a set of nonnegative integers (three per atom), and  $\epsilon$  is the fixed difference between energy levels of each oscillator.

**Limitations:** The Einstein model only works well for monatomic solids at temperatures above 100 K or so (the exact limit depends on the solid).

**solid.**

The basic point of equation T4.5 is that we will model a crystalline solid containing  $N$  identical atoms as if it contained  $3N$  identical independent quantum harmonic oscillators, each of which can store an integer number  $n_i$  of energy units  $\epsilon \equiv h\omega$ . We will call any solid accurately described by this model an **Einstein solid**.

Note that  $\epsilon \equiv h(k_s/m)^{1/2}$ , where  $k_s$  is the effective spring constant of the interactions holding an atom to its equilibrium position in the solid,  $m$  is the mass of the atom, and  $h$  is Planck's constant  $h$  over  $2\pi$ . Thus  $\epsilon$  increases as the strength of the interatomic forces increases and decreases as the atomic mass increases.

From this section to the end of chapter T5, we will focus on learning what we can about the thermal behavior of this particular model for a solid. Why focus on this model, and not, say, the ideal gas model? The answer is that it is *much* easier to determine the number of microstates corresponding to each macrostate for an Einstein solid than for any other reasonably realistic model. This in turn makes it comparatively easier to determine what statistical physics predicts about this model. However, models of other complex systems (including the ideal gas model) are *qualitatively* similar to this

## T4.3 Counting Microstates

Why focus on Einstein solids?

The thermal energy of an Einstein solid

The quantum zero-point energy of the solid is irrelevant



model, so what we learn from close inspection of this model applies in qualitative terms at least to other systems as well (as we will discuss in chapter T6).

To describe the macrostate of an Einstein solid, it is sufficient to specify the number of atoms  $N$  and its total internal energy  $U$ . Why? Empirically, we know that  $U = 3Nk_B T$  for a monatomic solid, so if we know  $U$ , we know  $T$ . We assume in the Einstein model that each atom occupies a fixed volume independent of the applied pressure  $P$  and is independent of other atoms, so  $P$  is irrelevant and we can calculate  $V$  directly from  $N$ . (The volume of a typical *real* solid depends only very weakly on temperature and pressure, so our model is a reasonably good approximation.) Therefore,  $N$  and  $U$  describe everything we need to know about the solid at the macroscopic level. (That we need *three* variables instead of two to describe the macrostate of an ideal gas is one of the things that makes that model more complicated than the Einstein solid for our purposes here.)

To describe a microstate of the solid, we have to specify an integer value  $n_i$  for each of the solid's  $3N$  independent oscillators. In general there will be *many* microstates (i.e., many distinct sets of values for all  $3N$  integers  $n_i$ ) that have the same total  $U$ . The number of possible microstates corresponding to the same given macrostate is called the **multiplicity**  $\Omega$  of that macrostate. In the case of an Einstein solid, where the macrostate is specified by  $U$  and  $N$ ,

$$\Omega(N, U) \equiv \text{multiplicity of macrostate specified by } U \text{ and } N$$

$$= \text{number of } N\text{-atom microstates having total energy } U \quad (\text{T4.6})$$

### Counting microstates

Examples of counting microstates for small  $U$ ,  $N$

In a solid of macroscopic size,  $3N$  will be on the order of magnitude of  $10^{23}$ , but let us start small. Imagine we have an Einstein solid consisting of a *single* atom, that is, *three* independent oscillators. (Of course, a single atom will have no lattice in which it can oscillate, but let us just pretend that this makes sense. We'll work up to larger numbers of atoms shortly.) We can describe the microstate of this system by specifying energy-level integers for each of the three oscillators (i.e., how many marbles each of these three bins contains). Let us write these numbers as a triplet of digits; for example, the triplet 032 specifies the microstate in which the first oscillator has 0 units of energy, the second has 3 units, and the third has 2 units. The total energy contained in the system in this case is  $U = 5\varepsilon$ . Other possible microstates corresponding to this macrostate are 320, 230, 302, 203, 023, 113, 311, 131, 041, 014, etc.

So let us start counting microstates for various different macrostates of this hypothetical one-atom Einstein solid. First, imagine that the total energy of the solid has its lowest possible value  $U = 0$ . There is only one microstate (000) compatible with this total energy, so we say that the multiplicity of this macrostate is  $\Omega(N, U) = \Omega(1, 0\varepsilon) = 1$ .

Now imagine that the total energy of the solid is  $U = \varepsilon$  (that is, the solid contains exactly 1 unit of energy). The microstates compatible with this total energy are 100, 010, and 001, for a total of three. The multiplicity of this macrostate is thus  $\Omega(1, 1\varepsilon) = 3$ .

Describing the macrostate of an Einstein solid

Definition of multiplicity



## Exercise T4X.1

Now imagine that the total energy of the solid is  $U = 2\epsilon$ . The multiplicity of this macrostate turns out to be  $\Omega(1, 2\epsilon) = 6$ . Write down the triplets for the six microstates corresponding to this macrostate.

## Exercise T4X.2

Now imagine that the total energy of the solid is  $U = 3\epsilon$ . What is the multiplicity of this macrostate? (Write down all possible microstate triplets consistent with this macrostate and count them.)

Similarly,  $\Omega(1, 4\epsilon) = 15$ ,  $\Omega(1, 5\epsilon) = 21$ , and  $\Omega(1, 6\epsilon) = 28$ .

An Einstein solid consisting of two atoms (six independent oscillators)

and zero total energy has one microstate 000000, so  $\Omega(2, 0\epsilon) = 1$ . If it has a

total energy of  $U = \epsilon$ , then the six possible microstates are 000001, 000010,

000100, 001000, and 100000, meaning that  $\Omega(2, 1\epsilon) = 6$ . If it has a

total energy of  $U = 2\epsilon$ , then the possible microstates are 000002, 000020,

000200, 002000, and 200000; and 000011, 000101, 001001, 010001,

100001, 000110, 001010, 010010, 011000, 100010, 100100,

101000, and 110000, for a total of 21 states, so  $\Omega(2, 2\epsilon) = 21$ . In a similar fash-

ion, you can determine that  $\Omega(2, 3\epsilon) = 56$ ,  $\Omega(2, 4\epsilon) = 126$ , and so on.

You can see that this counting of microstates gets pretty tedious after a

while. There is in fact a general formula for the number of microstates for a

given system. If  $q = U/\epsilon$  is the total number of energy units to be distributed

among  $3N$  oscillators, then the multiplicity of the macrostate is

$$\Omega(N, U) = \frac{(q + 3N - 1)!}{q!(3N - 1)!} \quad (\text{T4.7})$$

**Purpose:** This equation specifies the multiplicity  $\Omega$  of a macrostate

of an Einstein solid.

**Symbols:**  $N$  is the number of atoms in the solid;  $U$  is its total

energy;  $q \equiv U/\epsilon$  is the number of units of energy to be distributed

among the atoms;  $n!$  or  $n$  factorial  $\equiv 1 \cdot 2 \cdot 3 \cdots (n - 1) \cdot n$ .

**Limitations:** This equation only applies to an Einstein solid.

(The derivation of this formula is discussed in problem T4S.8.) So, for example,

$$\Omega(2, 4\epsilon) = \frac{(4 + 6 - 1)!}{4!6!} = \frac{4!5!}{9!} = \frac{(4 \cdot 3 \cdot 2 \cdot 1)(5 \cdot 4 \cdot 3 \cdot 2 \cdot 1)}{9 \cdot 8 \cdot 7 \cdot 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1} = \frac{9 \cdot 8 \cdot 7 \cdot 6}{4 \cdot 3 \cdot 2 \cdot 1} = 9 \cdot 7 \cdot 2 = 126 \quad (\text{T4.8})$$

## Exercise T4X.3

(a) Check that formula T4.7 yields the same results for  $\Omega(1, 0)$ ,  $\Omega(1, \epsilon)$ ,  $\Omega(1, 2\epsilon)$ , and  $\Omega(2, 2\epsilon)$  that we found earlier by direct counting. (b) Use formula T4.7 to verify that  $\Omega(1, 6\epsilon) = 28$ . (c) If an Einstein solid has three atoms, what is the multiplicity of the macrostate where it has 8 units of energy?



T4.4    Two Einstein Solids in Thermal Contact

Suppose that we now bring two Einstein solids  $A$  and  $B$ , one with  $N_A$  atoms (three  $N_A$  oscillators) and one with  $N_B$  atoms (three  $N_B$  oscillators), into thermal contact, so that microscopic interactions between atoms on the surfaces in contact can allow energy to flow between the solids. What we would like to understand, however, is how these solids will behave *macroscopically* after being brought into contact.

The macrostate of solid  $A$  is specified by  $N_A$  and  $U_A$ , while the macrostate of solid  $B$  is specified by  $N_B$  and  $U_B$ . Since  $N_A$  and  $N_B$  are fixed, the macrostates of  $A$  and  $B$  are essentially determined by their respective energies  $U_A$  and  $U_B$ . If the combined system of the two solids is thermally isolated, its total energy  $U = U_A + U_B$  is fixed (by conservation of energy); but at least in principle, the energies  $U_A$  and  $U_B$  of the two solids could have any values consistent with that total. For example, if the combined system's total energy is  $U = 6\epsilon$ , then possible pairs of values for  $U_A$  and  $U_B$  include  $U_A = 0$  and  $U_B = 6\epsilon$ , or  $U_A = 2\epsilon$  and  $U_B = 4\epsilon$ , or  $U_A = 5\epsilon$  and  $U_B = \epsilon$ , and so on.

Let us call a given pair of macrostates for solids  $A$  and  $B$  that are consistent with a fixed value of  $U = U_A + U_B$  a **macropartition** of the combined system for that  $U$ . For example, the pair of macrostates where  $U_A = 2\epsilon$  and  $U_B = 4\epsilon$  is one possible *macropartition* of the combined system for  $U = 6\epsilon$ .

Different macropartitions of the combined system of two solids therefore amount to different ways that the energy can be *macroscopically* divided (or "partitioned") between the solids. There is a real distinction to be made here between a *macropartition* and a *microstate* of the combined system. A *microstate* of the combined system specifies exactly how much energy *each individual oscillator* in both solids has. A macropartition, on the other hand, only specifies the *macroscopic* total energies  $U_A$  and  $U_B$  that the two macroscopic solids have, something we can measure macroscopically. In other words, we describe a macropartition of a combined system of two subsystems by describing the *macrostate* of each subsystem.

It is easiest to illustrate these ideas with a specific example. Suppose we bring two hypothetical one-atom solids into thermal contact. Imagine that their total combined energy is  $U = 6\epsilon$ . The **macropartition table** T4.1 lists all possible macropartitions for a combined system with this total energy.

A macropartition table for Einstein solids in contact

The *macropartition* of a pair of objects in thermal contact

Table T4.1    Possible macropartitions for $N_A = N_B = 1$ , $U = 6\epsilon$					
Macropartition	$U_A$	$U_B$	$\Omega_A$	$\Omega_B$	$\Omega_{AB}$
0:6	0	6	1	28	28
1:5	1	5	3	21	63
2:4	2	4	6	15	90
3:3	3	3	10	10	100
4:2	4	2	15	6	90
5:1	5	1	21	3	63
6:0	6	0	28	1	28
Grand total number of microstates = 462					



The numbers under the columns labeled  $U_A$  and  $U_B$  specify the macrostates of solids  $A$  and  $B$  by specifying the total energy of each solid in units of the basic energy unit  $\epsilon$ . Each number under the heading  $\Omega_A$  states the multiplicity of solid  $A$  when it has the specified energy  $U_A$ , and each number under the heading  $\Omega_B$  states the same for solid  $B$ . The value of  $\Omega_{AB}$  specified for each macropartition is the total multiplicity of the combined system in that macropartition (i.e., the total number of distinct microstates available to the system as a whole in that macropartition). This total multiplicity  $\Omega_{AB}$  is the product of  $\Omega_A$  and  $\Omega_B$ .

$$\Omega_{AB} = \Omega_A \Omega_B \quad (\text{T4.9})$$

because for each one of the  $\Omega_A$  possible microstates for solid  $A$ , there are  $\Omega_B$  possible microstates for solid  $B$ . For example, in the macropartition 3:3, the possible microstates of solid  $A$  are (in our previous notation) 300, 030, 003, 210, 201, 021, 120, 102, 012, and 111, and the possible microstates of system  $B$  are the same. The possible microstates of the combined system are as follows (the triplets on the left and right specify the microstates of solids  $A$  and  $B$ , respectively): 300-300, 300-030, 300-003, 300-210, 300-201, 300-021, 300-120, 300-102, 300-012, 300-111, 030-300, 030-030, 030-003, 030-210, and so on, for a total of  $10 \times 10 = 100$  distinct microstates.

### Exercise T4X.4

Prepare an analogous table for the case where  $N_A = N_B = 1$  and  $U = 8\epsilon$ . (Most of the multiplicities  $\Omega_A$  and  $\Omega_B$  you can copy from table T4.1; use equation T4.7 to calculate the rest.)

## T4.5 The Fundamental Assumption

In a more familiar system such as the ideal gas model, it is obvious that the gas will continually and randomly shift from microstate to microstate as the molecules collide with the walls and one another and exchange energy. A similar situation will apply here if we assume that the elementary oscillators in each solid weakly interact with one another: not so strongly that the approximation that the oscillators are independent becomes invalid, but strongly enough that energy is freely interchanged between the oscillators. Energy will also be shifted randomly back and forth across the boundary between the solids through the interactions of the oscillators on the surfaces in contact.

In short, as time passes, the combined system of two solids will randomly shift between different microstates consistent with the constraint that the total energy have some fixed value  $U$ . This means that under some circumstances, the macropartition of the combined system might fluctuate as the system randomly samples microstates in different macropartitions. For example, in the situation considered in table T4.1, the combined system in microstate 012-300 (one of the microstates corresponding to macropartition 3:3) might evolve to 013-200 (one of the microstates corresponding to macropartition 4:2) by transfer of 1 unit of energy across the boundary. In time, this system will sample each of the 462 possible microstates, and thus each of the possible macropartitions.

## Fundamental assumption of statistical mechanics

Now comes the big question: Can we say something about which of the macropartitions are the ones that we are most likely to see if we peek at the system at various times? The answer is yes, if we are willing to accept a simple and plausible assumption about the behavior of such systems. This assumption is called the **fundamental assumption** of statistical mechanics:

All of a system's accessible microstates are equally likely in the

long run.

*Accessible* in this context means "consistent with the value of the total internal energy of the system in question."

This disarmingly simple postulate provides the foundation for understanding irreversible processes, as we will see in chapters T5 and T6. Note that even though this assumption is simple and plausible, its ultimate justification is that it correctly predicts the behavior of macroscopic systems.

The most important consequence of this principle for us is that the probability of occurrence of a given energy macropartition (consistent with the given total internal energy) is directly proportional to the number of microstates that indistinguishably generate that macropartition, that is, to the total multiplicity  $\Omega_{AB}$  of that macropartition.

For example, suppose that we were to take a large number of "snapshots" of the system of two Einstein solids described in table T4.1. The fundamental assumption means that we would find the system to be in macropartition 3:3 in about  $100/462 = 0.216 = 21.6\%$  of the pictures and in macropartition 0:6 (or macropartition 6:0) in about  $28/462 = 0.061 = 6.1\%$  of the pictures and so on. Note that macropartition 3:3, the macropartition for which the energy is shared equally between the two identical solids, is the single most probable macropartition of the system.

## Exercise T4X.5

(a) Compute the probabilities of each of the macropartitions in table T4.1, and write them to the right of the value of  $\Omega_{AB}$  for that macropartition. (b) Do the same for the table that you constructed in exercise T4X.4. (c) Which macropartition in the latter case is the most probable one?

## T4.6 Using StatMech

Doing the calculations required to set up a table such as table T4.1 can be very tedious, particularly as the number of atoms in each solid becomes large. Fortunately, you can download a free computer program called StatMech that does all the calculations for you. This program is available in both Macintosh and Windows versions; go to the *Six Ideas* website (whose URL is given in this book's preface) and follow the links to the computer programs page.

When you run the program, it displays a window that looks something like that shown in figure T4.2 (except without the table). In the text boxes at the top of the window, you can enter the number of atoms you want in solids A and B and the total energy  $U$  that these solids will share (expressed as a multiple of the basic energy unit  $\epsilon$ ). If you then press the Calculate button, the program displays a table in the lower part of the window, shown in

Basic instructions for using StatMech



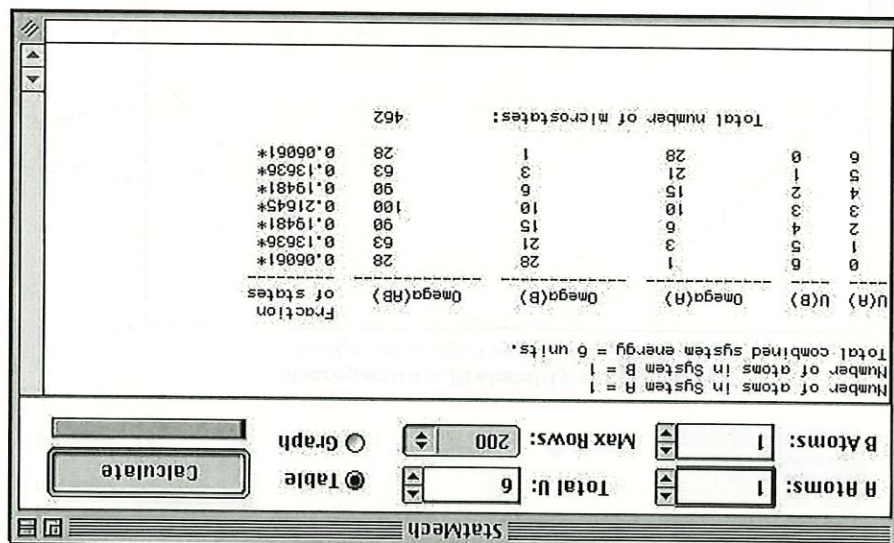


figure T4.2. You can print this table using the Print command under the File menu, or you can select all or part of the table and paste it into a word processing program.

Note that the final column of the table lists the number of microstates for each macrostate expressed as a fraction of the total number of accessible microstates. According to the fundamental assumption of statistical mechanics, this is also the probability of that macrostate's occurring. The stated macropartitions have probabilities above 0.0001; this means that the stated macrostates embrace about 99.98% of the system's total microstates.

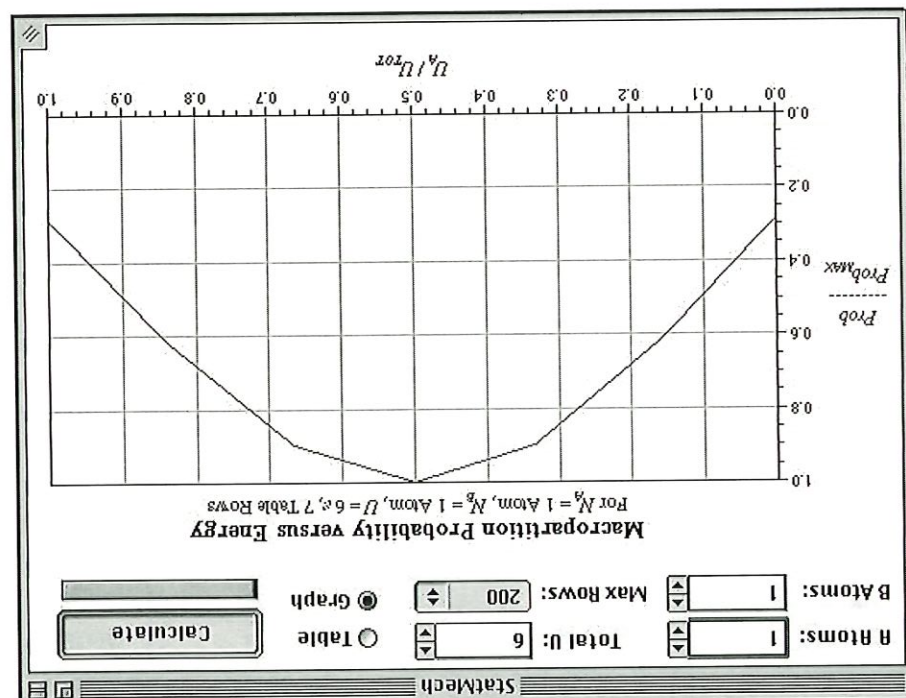
In principle, you can do by hand what StatMech does, at least when  $N_A$ ,  $N_B$ , and  $U$  are reasonably small (indeed, you did this in exercises T4X.4 and T4X.5). Once you have constructed a few tables on your own, however, you will appreciate how rapidly and easily the program generates tables.

Once you have calculated a table, you can also display a graph of the macropartition probabilities as a function of  $U_A$  by pressing the Graph radio button. The graph corresponding to the table in figure T4.2 is shown in figure T4.3.

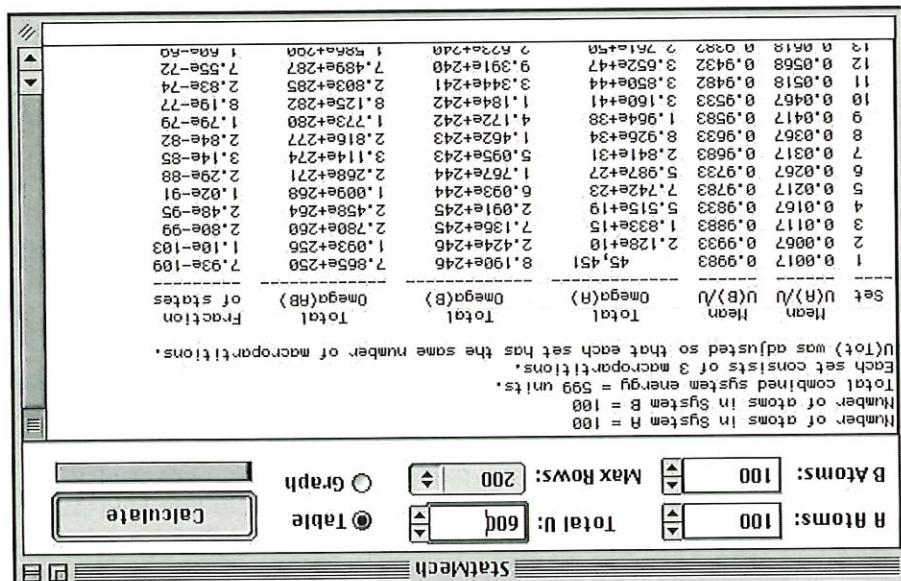
You can enter fairly large numbers for  $N_A$  and  $N_B$  without any problem. If you enter numbers for  $U$  that are larger than the Max Rows (maximum number of table rows) value selected, each row of the table will display the summed results for a set of macropartitions instead of the results for an individual macropartition. The program does this so that the number of table rows does not become too unwieldy.

The table layout becomes somewhat different under these circumstances: Instead of columns for  $U_A$  and  $U_B$ , you will see columns specifying the set number (equivalent to the table row number) and the average values of the ratios  $U_A/U$  and  $U_B/U$  for the macropartitions in the set. An example is shown in figure T4.4. Under these circumstances, the program will only accept a value of  $U$  that is an integer multiple of Max Rows minus 1, so that the number of macropartitions in every bin is exactly the same. If you enter a number that is just an integer multiple of Max Rows instead of a multiple minus 1 (as I did in the case shown in figure T4.4), the program

How StatMech handles large values of  $U$



**Figure T4.2.** A graph of the relative macropartition probabilities for the table shown in figure T4.2.



This is how StatMech formats the macropartition table when the value for  $U$  exceeds Max Rows.



## TWO-MINUTE PROBLEMS

T4T.1

Consider a system consisting of two Einstein solids  $P$  and  $Q$  in thermal contact. Assume that we know the number of atoms in each solid and  $\epsilon$ . What do we know about the system if we also know the quantum state of each atom in each solid?

- A. Its macrostate
- B. Its microstate
- C. Its macropartition
- D. Its microstate and macropartition
- E. Its macrostate and macropartition
- F. Its macrostate and microstate
- T. Its macrostate, microstate, and macropartition

T4T.3

Consider a system consisting of two Einstein solids  $P$  and  $Q$  in thermal contact. Assume that we know the number of atoms in each solid and  $\epsilon$ . What do we know about the system if we also know the total

Consider a system consisting of two Einstein solids  $P$  and  $Q$  in thermal contact. Assume that we know the number of atoms in each solid and  $\epsilon$ . What do we know about the system if we also know the total energy in each of the two objects? (Please choose from the possible answers listed in problem T4T.1.)

T4T.2

(a) Run StatMech for the case where  $N_A = N_B = 1$  and  $U = 6\epsilon$ , and verify that the program reproduces table T4.1. Also have a look at the graph of macropartition probabilities. (b) Run the case where  $N_A = N_B = 10$  and  $U = 60\epsilon$ . What is different about the table (besides the fact that it is longer)? What is different about the graph? (c) Now scale everything up by a factor of 10 again, to  $N_A = N_B = 100$  and  $U = 600\epsilon$ . (Note that the program now begins to arrange macropartitions into bins.) What else has changed about the table? How has the graph changed? (d) Continue to increase the size of the system in steps of factors of 10 until the calculations start to take too long. Describe what you think are the important trends in terms of how the tables and graphs change as the size of the system increases.

## Exercise T4X.6

[Hint: Look at the table for a set of two solids with fairly large values of  $N_A$ ,  $N_B$ , and  $U$ . Imagine that we start out with solid  $A$  being very cold ( $U_A$  very small) and solid  $B$  being very hot ( $U_B \approx U$ ). What will happen as time passes and the pair of solids starts visiting microstates in adjacent macropartitions?]

Before you read chapter T5, I strongly recommend that you play with this program. First check that the program reproduces the results of exercises T4X.4 and T4X.5. Then try larger solids with larger total energies. Do some runs where the two solids have unequal sizes as well. This program plainly displays Boltzmann's resolution to the mystery of irreversibility, if you have the eyes to see it! See if you can figure it out *before* you read chapter T5. The truth is out there.

The truth about irreversibility is out there . . .

assumes that you really meant the number typed minus 1. (Specifying a value for  $U$  that is bigger than Max Rows but is not an integer multiple of Max Rows or an integer multiple minus 1 generates an error message when you press Calculate.)

For more complete (and/or up-to-date) instructions, select About StatMech (under the Apple menu on Macintosh systems or under the Edit menu on Windows systems).

energy of the combined system? (Please choose from the possible answers listed in problem T4T.1.)

**T4T.4** What is the *crucial* characteristic of an Einstein solid that makes it easier to analyze in the context of this chapter than most other kinds of thermodynamic systems?

- A. The atoms are arranged in a regular, cubic lattice.  
 B. The atoms are identical.  
 C. Its microstates are comparatively easy to count.  
 D. The atomic vibration energy levels are equally spaced.  
 E.  $\Omega(U, N)$  is always reasonably small.  
 F. Other (specify).

**T4T.5** The zero-point energy of an Einstein solid can be ignored because

A. It is zero.  
 B. It never changes in any thermal interaction.  
 C. It is insignificant compared to the solid's total energy.

- D. It is just a quantum-mechanical effect.  
 E. Other (specify).

**T4T.6** The multiplicity of an Einstein solid with 3 atoms and 4 units of energy is

A.  $4.8 \times 10^8$   
 B. 715  
 C. 495  
 D. 36  
 E. 12  
 F. Other

**T4T.7** Which of the following statements is true?

A. There are always many microstates in a macrostate.  
 B. All accessible macrostates are equally probable.  
 C. All microstates of a system are equally probable.  
 D. All accessible macrostates are equally probable.  
 E. When two objects in thermal contact are isolated from everything else, their macrostates cannot change.  
 F. None of the above.

## Basic Skills

**T4B.1** Imagine that we have an ideal gas consisting of 15 molecules. We can flip the signs of each of the three velocity components of a given molecule without changing its overall energy (and thus without changing the gas's macrostate). How many possible patterns of sign choices are there?

**T4B.2** Calculate the multiplicity of an Einstein solid with  $N = 1$  and  $U = 6\epsilon$  by directly listing and counting the microstates. Check your work by using equation T4.7.

**T4B.3** Calculate the multiplicity of an Einstein solid with  $N = 1$  and  $U = 5\epsilon$  by directly listing and counting the microstates. Check your work by using equation T4.7.

**T4B.4** Use equation T4.7 to calculate the multiplicity of an Einstein solid with  $N = 4$  and  $U = 10\epsilon$ .

**T4B.5** Use equation T4.7 to calculate the multiplicity of an Einstein solid with  $N = 3$  and  $U = 15\epsilon$ .

**T4B.6** How many times more likely is it that the combined system of solids described in table T4.1 will be found in macropartition 3:3 than in macropartition 0:6, if the fundamental assumption is true?

**T4B.7** How many times more likely is it that the combined system of solids described in table T4.1 will *not* be

## Synthetic

**T4S.1** Consider an Einstein solid consisting of  $N_A = 1$  atom (three oscillators). Each oscillator can store any integer number of energy units  $\epsilon$ . The following table lists the number of microstates  $\Omega_A$  available to the solid when it has various values of total thermal energy  $U_A$ .

$U_A$	0	$1\epsilon$	$2\epsilon$	$3\epsilon$	$4\epsilon$	$5\epsilon$	$6\epsilon$	$7\epsilon$	$8\epsilon$	$9\epsilon$	$\Omega_A$
	1	3	6	10	15	21	28	36	45	55	

By actually listing and counting the various possible microstates, verify the results for the multiplicity  $\Omega_A$  for the cases where  $U_A = 4\epsilon$  and  $U_A = 7\epsilon$ . (You can check your results by using equation T4.7.)

**T4S.2** Consider an Einstein solid consisting of  $N_B = 2$  atoms. The following table lists the number of microstates  $\Omega_B$  available to the solid when it has various values of total internal energy  $U_B$ .

$U_B$	0	$1\epsilon$	$2\epsilon$	$3\epsilon$	$4\epsilon$	$5\epsilon$	$6\epsilon$	$7\epsilon$	$8\epsilon$	$9\epsilon$	$\Omega_B$
	1	6	21	56	126	252	462	792	1287	2002	

## HOMEWORK PROBLEMS



- (a) By actually listing the various possible microstates, verify the result for  $U_B = 2\epsilon$ .  
 (b) Using equation T4.7, verify the value of  $\Omega_B$  for  $U_B = 6\epsilon$  and  $9\epsilon$ .

**T4S.3**

Imagine putting the two solids discussed in problems T4S.1 and T4S.2 into thermal contact. Imagine that the resulting combined system is isolated from everything else, and that the combined system contains 6 units of energy (that is,  $U_A + U_B = 6\epsilon$ ).

- (a) Construct a table showing  $U_A$ ,  $U_B$ ,  $\Omega_A$ ,  $\Omega_B$ , and  $\Omega_{AB}$  for all possible macrostates of the system (i.e., a table analogous to table T4.1), and compute the probabilities for each of the seven possible macrostates according to the fundamental assumption.  
 (b) Identify the most probable macrostate(s) of this system. Is the energy evenly divided between the solids in the most probable macrostate(s)?

**T4S.4**

Imagine putting the two solids discussed in problems T4S.1 and T4S.2 into thermal contact. Imagine that the resulting combined system is isolated from everything else, and that the combined system contains 9 units of energy (that is,  $U_A + U_B = 9\epsilon$ ).

- (a) Construct a table showing  $U_A$ ,  $U_B$ ,  $\Omega_A$ ,  $\Omega_B$ , and  $\Omega_{AB}$  for all possible macrostates of the system (i.e., a table analogous to table T4.1), and compute the probabilities for each of the 10 possible macrostates according to the fundamental assumption.  
 (b) Identify the most probable macrostate(s) of this system. Is the energy evenly divided between the solids in the most probable macrostate(s)?

**T4S.5**

Imagine putting two solids with  $N_A = N_B = 2$  in thermal contact, and imagine that the resulting combined system is isolated from everything else and that it contains 9 units of energy (that is,  $U_A + U_B = 9\epsilon$ ).

- (a) Construct a table showing  $U_A$ ,  $U_B$ ,  $\Omega_A$ ,  $\Omega_B$ , and  $\Omega_{AB}$  for all possible macrostates of the system (i.e., a table analogous to table T4.1), and compute the probabilities for each of the 10 possible macrostates according to the fundamental assumption.  
 (b) Identify the most probable macrostate(s) of this system. Is the energy evenly divided between the solids in the most probable macrostate(s)?

**T4S.6**

Use StatMech to generate a macropartition table for the situation where  $N_A = N_B = 5$  and  $U = 20\epsilon$ , and answer the following questions. (1) How many total microstates are available to the system? (2) Which is the most probable macrostate, and how many microstates are available to the system in this macrostate? (3) What is the average energy per atom in each solid in this macrostate? (4) What range of values of the ratio  $U_A/U$  corresponds to macropartitions

- (a) Answer the same set of questions as in (a) for the case where  $N_A = N_B = 50$  and  $U = 200\epsilon$ . (Note that I am scaling all variables up by a factor of 10 each time, so that the energy per atom remains fixed.)  
 (b) Carefully and completely describe any trends you see in how the answers to these questions change as the system becomes larger.

**T4S.7**

- (a) Use StatMech to generate tables for the following five different cases: (1)  $N_A = N_B = 50$ , (2)  $N_A = 40$  and  $N_B = 60$ , (3)  $N_A = 30$  and  $N_B = 70$ , (4)  $N_A = 20$  and  $N_B = 80$ , and (5)  $N_A = 10$  and  $N_B = 90$ . Choose  $U = 200\epsilon$  in all cases. In each case, compare the energy per atom for each solid (i.e., compare  $U_A/N_A$  to  $U_B/N_B$ ) when the system is in the most probable macrostate. (You can see the big picture pretty quickly if you look at the graphs of macropartition probabilities; look at the table for details.) State a simple rule describing how  $U_A/N_A$  is related to  $U_B/N_B$  in the most probable macrostate. Is your rule always exactly true?  
 (b) How does your rule fare when you increase all numbers by a factor of 100? Support your response with some evidence.

**T4S.8**

We can derive equation T4.7 as follows. First, note that the problem of counting the microstates of an Einstein solid is essentially the same as the problem of finding the number of distinct patterns that can be generated by pulling marbles and matchsticks randomly from a bag. For example, imagine that we pull the following sequence of items from the bag (reading from left to right):



If we imagine each marble to be a unit of energy and each matchstick to be a division between two oscillators, then this pattern corresponds to the 130211 microstate for an Einstein solid with  $N = 2$  atoms (six oscillators) and  $U = 8\epsilon$ .

- (a) Argue that a solid with  $M$  oscillators and  $q$  units of energy will be represented by  $q$  marbles and  $M - 1$  matches.  
 (b) Argue that if we put  $M - 1$  matches and  $n$  marbles in the bag, there will be a total of  $(M + q - 1)!$  different ways of pulling objects out of the bag. (Hint: When we select the first object, we have  $M + q - 1$  choices. When we choose the second item, we now only have  $M + q - 2$  choices, since we've already pulled out one object, and so on.)  
 (c) Not all these distinct ways of pulling out objects generate distinct patterns. For example, consider



## Rich-Context

## T4R.1

Consider a hypothetical system in which each atom can only be in one of two quantum states, a ground state with energy 0 or an excited state with energy  $\epsilon$ . The atoms have fixed positions and fixed volumes, and there is no way for an atom to change its energy except by going from the ground state to the excited state or vice versa. As with the Einstein solid, we can completely describe the macrostate of this system by specifying the number of atoms  $N$  and their total thermal energy  $U$ .

(a) Find an expression, in terms of  $U$  and  $N$ , for the number of atoms  $n$  that are in the excited state. Find a formula for the multiplicity  $\Omega(U, N)$  of a macrostate where the system has  $N$  atoms and total energy  $U$ . (*Hints:* Play around with small systems first. For example, imagine that we have  $N = 3$  and  $U = 2\epsilon$ . We might describe the possible microstates as being 011, 101, and 110. Once you have developed some sense about the multiplicity of small systems, start working on a general formula, which will involve some factorials. Once you have a trial formula, go back and check it in small-system cases where you can directly count the microstates.)

of energy.

(d) Argue finally that equation T4.7 correctly states the number of distinct patterns that can be generated, and thus the number of distinct microstates of an Einstein solid with  $M$  oscillators and  $n$  units of energy.

## ANSWERS TO EXERCISES

T4X.1 011, 101, 110, 200, 020, 002

T4X.2 111, 012, 021, 102, 201, 120, 210, 003, 030, and 300, so  $\Omega(1, 3\epsilon) = 10$ T4X.3  $\Omega(3, 8\epsilon) = 12,870$ 

T4X.4 The table is as follows:

Macropartition	$U_A$	$U_B$	$\Omega_A$	$\Omega_B$	$\Omega_{AB}$
0:8	0	8	1	45	45
1:7	1	7	3	36	108
2:6	2	6	6	28	168
3:5	3	5	10	21	210
4:4	4	4	15	15	225
5:3	5	3	21	10	210
6:2	6	2	28	6	168
7:1	7	1	36	3	108
8:0	8	0	45	1	45

Grand total number of microstates = 1287

## Advanced

## T4A.1

(a) Show that if you take the time derivative of equation T4.1, you get

$$0 = v_x(ma_x + k_s x) + v_y(ma_y + k_s y) + v_z(ma_z + k_s z)$$

(T4.10)

(b) By changing initial conditions, I could arrange it so that  $v_x$ ,  $v_y$ , and  $v_z$  have any values I please at a given time. Argue that since this equation has to be zero at *all* times, the quantities in parentheses have to be *independently* equal to zero at all times. (c) Show that each of these quantities in parentheses is the same as Newton's second law for a simple one-dimensional harmonic oscillator moving in the corresponding axis direction.

(c) Construct a macropartition table for a system consisting of two subsystems with  $N_A = 20$ ,  $N_B = 20$ , and  $U = 8\epsilon$ . Does it look at least qualitatively like the macropartition tables we have been constructing for Einstein solids? Explain. *Comment:* This model is also actually a pretty good description of certain kinds of solids at very low temperatures when they are placed in a strong magnetic field. Under such circumstances, the magnetic moment of an atom in the solid can be either aligned with the field (which we can take to be the ground state) or anti-aligned with the field (which we can take to be the excited state). It is also easier to determine multiplicities for this model than for the Einstein solid. So why do we not focus on this model instead of on the Einstein solid? This model only applies to pretty esoteric systems. Even worse, it exhibits peculiar behavior when its energy is such that  $n > \frac{1}{2}N$ , behavior that is almost never seen in nature otherwise. Therefore, unlike the Einstein solid, this model is not very useful for helping us understand how normal complex systems behave.



**T4X.5** The probabilities are as follows:

**Table T4.1**

Macro-partition	Probability
0:6	0.061
1:5	0.136
2:4	0.195
3:3	0.216
4:2	0.195
5:1	0.136
6:0	0.061

**Exercise T4X.4**

Macro-partition	Probability
0:8	0.035
1:7	0.084
2:6	0.131
3:5	0.163
4:4	0.175
5:3	0.163
6:2	0.131
7:1	0.084
8:0	0.035

The 4:4 macropartition is the most probable one in the list for the situation in exercise T4X.4.

**T4X.6** You should find that as the systems get larger, (1) both the multiplicity associated with each row of the table and the total number of microstates available to the system become *extremely* large, (2) the most probable macropartition is always where the energy is split evenly between the two systems, but (3) the width of the peak on the macropartition probability graph becomes smaller and smaller as the system size increases. This means that for large systems, the vast majority of microstates are within macropartitions very close to the most probable macropartition.

## Chapter Overview

### Introduction

This is the core chapter of the unit. In this chapter, we will develop further the ideas introduced in chapter T4, using StatMech to create macropartitions for larger and larger Einstein solids. In doing so, we will finally discover how random microscopic processes lead to irreversible behavior in macroscopic systems. We will also learn how a system's *entropy* conveniently characterizes and quantifies its irreversible behavior.

### Section T5.1: What Happens as Systems Become Large?

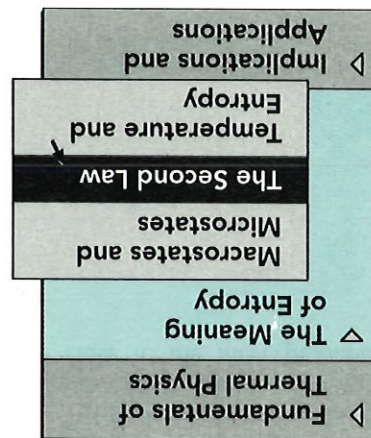
Using StatMech, we can easily create macropartition tables for large Einstein solids sharing many units of energy. We find that as the numbers become large, (1) the number of microstates available to the system becomes *extremely* (almost incomprehensibly) huge, but (2) the vast majority of microstates are in an increasingly narrow range of macropartitions around the most probable macropartition, so that a graph of macropartition probability versus energy in either solid becomes a very narrow spike.

### Section T5.2: Irreversibility in Einstein Solids

This implies that (1) if the combined system is *not* very near the most probable (equilibrium) macropartition initially, random energy transfers will inevitably move it toward that macropartition; and (2) it will subsequently *stay* very close to that macropartition (exhibiting only tiny fluctuations away from it), in spite of the random energy transfers between the two solids. This is so because *that is where the microstates are*. The number of microstates available to the system increases so incredibly rapidly as the system moves toward equilibrium that while it is possible in principle for a random energy transfer to move the system away from equilibrium, it is so unbelievably unlikely as to be impossible for all practical purposes. (This section uses a number of StatMech-generated quantitative examples to drive home the point.) Therefore, microscopically random energy transfers lead quite naturally to essentially irreversible shifts in the system's macroscopic properties!

### Section T5.3: Irreversibility in General

We have been using Einstein solids as our core example because it is easy to determine the multiplicity of a combined system of two such solids. But the argument does not depend on the exact values of the multiplicity: it applies to *any* system of objects whose multiplicities are extremely rapidly increasing functions of their thermal energies. This applies to the vast majority of physical objects (indeed, I chose to discuss Einstein solids precisely because their behavior is so typical). Understanding how irreversibility arises in Einstein solids therefore gives us at least qualitative insight into how virtually all other objects behave.





## Section T5.4: The Definition of Entropy

We define a system's entropy  $S$  in a given macrostate to be

**Purpose:** This equation defines the entropy  $S$  of a thermodynamic system in a given macrostate.  
**Symbols:**  $S$  is the macrostate's multiplicity;  $k_B$  is Boltzmann's constant.  
**Limitations:** There are none; this is a definition. However, it is difficult to determine  $S$  exactly in many situations.

The entropy  $S$  is simply a different way to specify a system's multiplicity  $\Omega$ , but it has several advantages over specifying the multiplicity directly: (1) the logarithm converts extremely large multiplicities to more manageable sized entropies; and (2) when we put two systems in contact, the total multiplicity is the *product* of the two systems' individual multiplicities, but the total entropy is the more convenient *sum* of the individual entropies:

$$S_{AB} = S_A + S_B \quad (\text{T5.7})$$

**Purpose:** This equation describes the total entropy  $S_{AB}$  for a given macropartition of a system consisting of two subsystems  $A$  and  $B$  in thermal contact.

**Symbols:**  $S_A$  and  $S_B$  are the subsystems' entropies in that macropartition.  
**Limitations:** There are none. This directly follows from the definitions of entropy and multiplicity.

## Section T5.5: The Second Law of Thermodynamics

So we see that random energy transfers between large systems in thermal contact essentially *never* move the combined system to a macropartition with a smaller multiplicity (and thus smaller total entropy). The second law of thermodynamics expresses this truth in a short, simple phrase: *The entropy of an isolated system never decreases.* This is one of the most important and useful laws in physics. However, one should always remember that this law (as we have seen) is a consequence of more fundamental principles (that all microstates are equally probable and that the multiplicities of most macroscopic objects increase incredibly rapidly with increasing energy).

## Section T5.6: Entropy and Disorder

Equation T5.7 links entropy to multiplicity. Popular treatments of entropy often link it to *disorder*. This often works because macrostates we consider to be "disordered" *usually* have greater multiplicities than states we consider "ordered" (e.g., there are many more ways for your room to be disordered than ordered). But this linkage can also be misleading: Sometimes macrostates that appear more orderly than others actually have more microstates (e.g., a glass filled with disorderly crushed ice has far *fewer* microstates than a glass containing the same mass of orderly appearing water). When in doubt, you should always remember that entropy is most fundamentally linked to multiplicity, not disorder.



## T5.1 What Happens as Systems Become Larger?

A quick review

In chapter T4 we developed the basic concepts of the field of physics known as *statistical mechanics*. Using the Einstein solid as the guiding example, we learned about the crucial distinction between *macrostates* and *microstates*. We learned that the multiplicity  $\Omega$  of a macrostate (the number of microstates consistent with that macrostate) can be a very large number. We learned to describe the *macropartitions* of a combined system by specifying the macrostates of its subsystems. We also saw that the fundamental assumption of statistical mechanics (that all accessible microstates are equally probable) implies that when energy is shuffled around randomly in a combined system, macropartitions with larger multiplicities will be more probable. These ideas provide the key to understanding irreversibility and the idea of entropy. The purpose of this chapter is to work through the consequences of the fundamental assumption (still in the context of Einstein solids) to discover how irreversible processes arise naturally out of the random shuffling of microstates.

StatMech enables us to study larger systems

It turns out that the irreversible nature of macroscopic processes depends crucially on the fact that an incredibly huge number of atoms are involved in any process where macroscopic objects interact. In chapter T4, we mostly considered interacting Einstein solids consisting of a few atoms sharing only a handful of units of energy, because only for small systems is it practical to do the calculations by hand. Yet even the smallest dust mote contains thousands of trillions of atoms.

The StatMech program introduced at the end of chapter T4 allows us to explore the behavior of larger solids than we can calculate by hand, although the number of atoms that the program can handle is still far smaller than any real solid would contain. Still, by running the program with an increasing number of atoms involved in each solid, we can spot trends that allow us to extrapolate to even larger numbers.

Larger systems have huge multiplicities

If you did the runs suggested in exercise T4X.6 or problem T4S.6 or T4S.7, you should have noted several things. First, you probably noticed that as  $N_A$ ,  $N_B$ , and  $U$  become large, the number of accessible microstates goes *through the roof*. For example, consider a system consisting of two Einstein solids with  $N_A = N_B = N$  (so that each solid is a tiny cube only 4 atoms on a side). When the total energy is  $U = 200\epsilon$ , StatMech tells us that there are a total of about  $2 \times 10^{161}$  microstates available to the system. Since there are very roughly  $10^{80}$  protons, neutrons, and electrons in the visible universe, if each proton, neutron, and electron in our universe itself contained a universe's worth of smaller particles, the total number of particles would *still* be more than a factor of 20 smaller than the total number of microstates here! The numbers only get more ridiculous as the systems grow in size. When  $N_A = N_B = 1,000,000$  (so that the solids are 100 atoms on a side) and  $U = 4,999,999\epsilon$ , StatMech tells us that the total number of microstates has increased to more than  $6 \times 10^{3,291,557}$ . Words cannot easily express how huge this number is: it would take about 750 single-spaced pages just to *write* this number without using scientific notation. Imagine what happens as we go to solids containing roughly  $10^{23}$  particles!

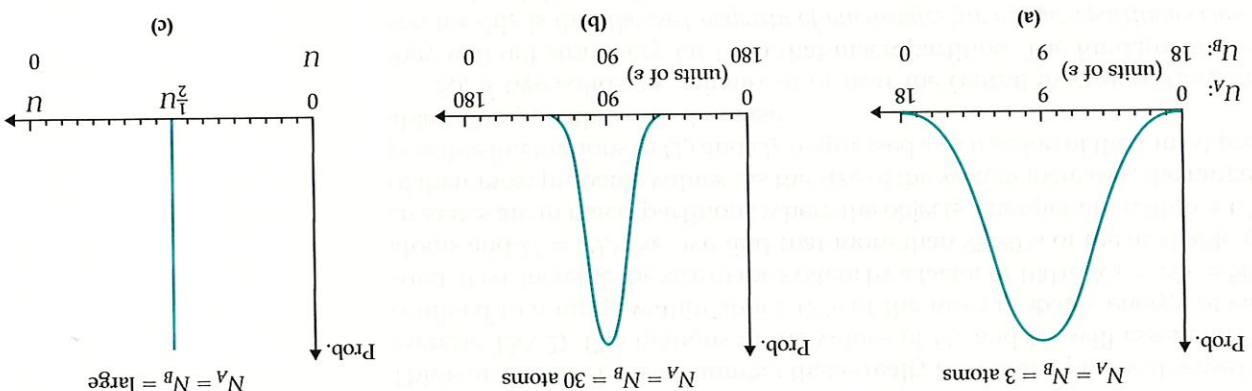
Larger systems have more sharply peaked probability graphs

Second, you may have noticed that the *shape* of the graph of macropartition probabilities changes as  $N_A$ ,  $N_B$ , and  $U$  become large. When  $N_A$ ,  $N_B$ , and  $U$  are small, the graph of probability versus macropartition is a fairly broad, bell-shaped curve, meaning that even the lowest-probability macropartitions have a significant probability of being seen if you watch the combined system long enough. As  $N_A$ ,  $N_B$ , and  $U$  get larger, though, the curve gets narrower.



Perhaps you can imagine that as these numbers get very large, the probability graph narrows to a spike of almost infinitesimal width (see figure T5.1).

Figure T5.1



How the graph of macropartition probability changes as a system gets larger.

## T5.2 Irreversibility in Einstein Solids

I claim that these results have two direct and very important implications:

1. If the combined system is *not* in the most probable macropartition to begin with, it will rapidly and inevitably move toward that macropartition.
2. It will subsequently *stay* at that macropartition (or very near to it), in spite of the random shuffling of energy back and forth between the two solids.

How do these statements follow from what we have observed?

Let us consider the second implication first. Imagine that our two Einstein solids have nearly the same energy before they are brought into contact. After they are brought into contact, they randomly shuffle energy around internally and across the boundary between them, sampling various possible microstates. The fundamental assumption implies that the probability that the system will end up in a given microstate after one of these shuffles is the same for all microstates, and since some microstates are in different macropartitions, the combined system's macropartition will fluctuate randomly in time. With a very small system (say,  $N_A = N_B = 5$  atoms and  $U = 20\epsilon$ ), these fluctuations can be pretty significant. Even if the system starts out near the center macropartition, there is about one chance in 10,000 that if we peek at the system at some later time, we will find it to have wandered into either one of the extreme macropartitions (where all the energy is in one solid and none in the other). We will see fluctuations of  $\pm 4\epsilon$  (which corresponds to almost  $\pm 40\%$  of the most probable value  $10\epsilon$  of the energy in each solid) quite commonly.

On the other hand, even in only a modestly larger system (e.g., with  $N_A = N_B = 50$  atoms and  $U = 200\epsilon$ ), the probability graph narrows significantly, and the probability of observing large fluctuations gets much smaller. For example, the probability of observing this system to be in its most extreme observable macropartition (where  $U_A = 0$  and  $U_B = 200\epsilon$ ) turns out to be

$$\Pr(U_A = 0) = \frac{\Omega_{AB}(U_A = 0)}{\Omega_{\text{grand total}}} \approx 3.88 \times 10^{-43} \quad (\text{T5.1})$$

Fluctuations around equilibrium are very small

This is an extremely small number that is really zero in any practical sense (see exercise T5X.2). Fluctuations in the values of  $U_A$  and  $U_B$  will essentially be confined to a range within about 17% of the most probable energy of each solid. If we increase the size of the system by a factor of 100 to  $N_A = N_B = 5000$  atoms and  $U = 19,999\epsilon$ , we find that more than 99.99% of the available microstates are in macropartitions where the objects' energies are within  $\pm 1.7\%$  of their most probable values. As the size of the system increases, the range of possible fluctuations in  $U_A$  and  $U_B$  (expressed as a fraction of their most probable values) continues to decrease.

So, if two solids are initially at or near the central macropartition, then they will not stray very far from that macropartition. The fundamental reason for this is that *the vast majority of microstates are in macropartitions close to the most probable one*. If each microstate is really equally probable, the system will seem to strongly prefer being in macropartitions *very* close to the most probable macropartition.

### Exercise T5X.1

Run StatMech and verify that the probability quoted in equation T5.1 is roughly correct. What is the probability that the system will be found in the 1 : 199 macropartition?

### Exercise T5X.2

The age of the universe is probably about  $1.4 \times 10^{10}$  y, and there are about  $3 \times 10^7$  s in 1 y. If you had been peeking at a system of two Einstein solids with  $N_A = N_B = 50$  atoms and  $U = 200\epsilon$  at 1 billion times per second from the day the universe began, roughly what would be the probability that you would have seen the system in its most extreme observable macropartition (0 : 200) by now? (The point is that even though it is *theoretically* possible for this macropartition to occur, it is *impossible* in any practical sense.)

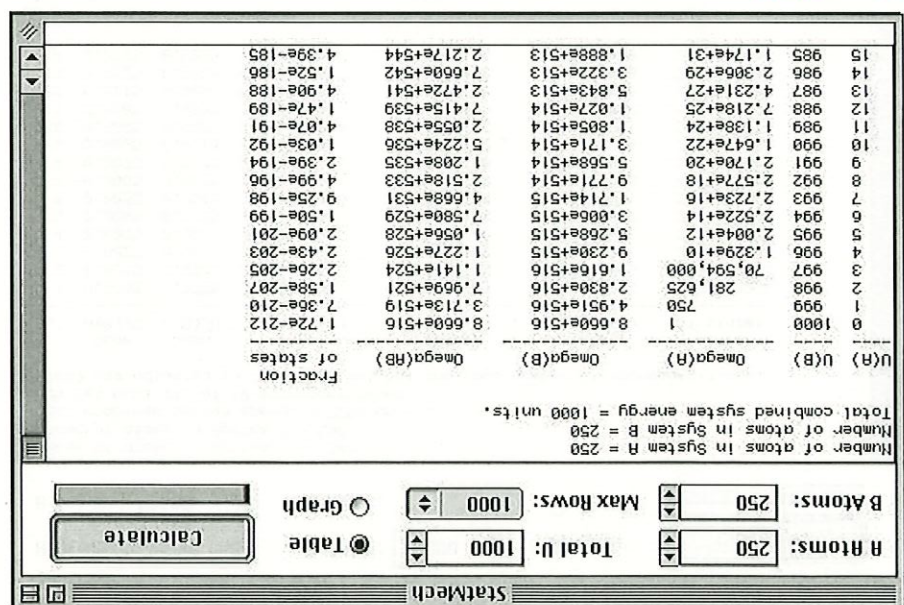
The inevitable march to equilibrium

Now imagine that we start with the solids in a fairly extreme macropartition. Once the solids are brought into thermal contact, they will begin to randomly shuffle energy back and forth, sampling new microstates. But the vast majority of microstates near the original macropartition are to be found in the direction toward the most probable macropartition, so the macropartition of the system will almost certainly move in that direction.

For example, consider the StatMech table shown in figure T5.2. Imagine in the situation shown (where  $N_A = N_B = 250$  atoms and  $U = 1000\epsilon$ ) that  $U_A = 12\epsilon = 0.012U$  and  $U_B = 988\epsilon = 0.988U$  when the solids are brought into contact at  $t = 0$ . This would correspond to solid A having a relatively low temperature initially and solid B having a relatively high temperature. Now, it takes some time for energy to flow by random processes from one solid into the other, so not all the system's theoretically possible microstates are actually "available" to the system at the instant when we put the two solids in contact. Let us say that we wait for whatever time interval is typically required for the total energy of the solid to shift by  $0.001U$  (= one energy unit  $\epsilon$  in this case) and then peek at the system again. What is the probability that we find that the "hot" solid B gave the unit of energy to the "cold" solid A rather than the other way round?

We can estimate this by making the crude assumption that *all* the microstates in the original macropartition and in the two adjacent macropartitions are equally probable and *no* microstates in *other* macropartitions are





possible at all. According to the table, the multiplicity of the macropartition below the initial one (the macropartition that results if B gives a unit of energy to A) is about  $2.5 \times 10^{541}$ . The multiplicity of the macropartition above the initial macropartition (the one that results if A gives a unit of energy to B) is about  $2.1 \times 10^{538}$ . This means that the probability that the hot solid B gains a unit of energy from the cold solid A compared to the probability of the reverse process is very roughly

$$\frac{\Pr(A \rightarrow B)}{\Pr(B \rightarrow A)} \approx \frac{\Omega_{AB}(U_A = 11e)}{\Omega_{AB}(U_A = 13e)} = \frac{2.1 \times 10^{538}}{2.5 \times 10^{541}} = 0.75 \times 10^{-30} \quad (\text{T5.2})$$

(Note that my calculator cannot handle exponents this large, so I calculated the ratio by dividing 2.1 by 2.5 to get 0.75 and then subtracted 541 from 538 to find the exponent.) So if the energies of solids A and B change by 1 unit, it is about 1200 times more likely that the hot one will give a unit of energy to the cold one (taking the system closer to equilibrium) than it is for that energy to flow the other way. Again, as the size of the system grows, these numbers grow more extreme. Let us scale the previous situation up by a factor of 10 (see figure T5.3). The row of the table closest to our previous initial condition is the row summarizing the 10 macropartitions whose average value of  $U_A$  is 0.0125U. An energy shift of about 0.001U in this case still means either going up one or down one table row. Again, assuming that all microstates in these rows are equally probable, the likelihood that this amount of energy will be found to have shifted from the cold solid to the hot solid compared to going the "right" way is

$$\frac{\Pr(A \rightarrow B)}{\Pr(B \rightarrow A)} \approx \frac{\Omega_{AB}(U_A \approx 0.0115U)}{\Omega_{AB}(U_A \approx 0.0135U)} = \frac{2.1 \times 10^{5423}}{4.3 \times 10^{5453}} = 0.5 \times 10^{-30} \quad (\text{T5.3})$$

We see that the probability that energy will flow from the hot object to the cold object is completely overwhelming. If we had been trying this experiment 1 billion times per second since the beginning of the universe  $4 \times 10^{17}$  s ago, the chance that we would have seen this much energy flow the wrong way even once in a system this tiny would still be only about 1 in 5000.

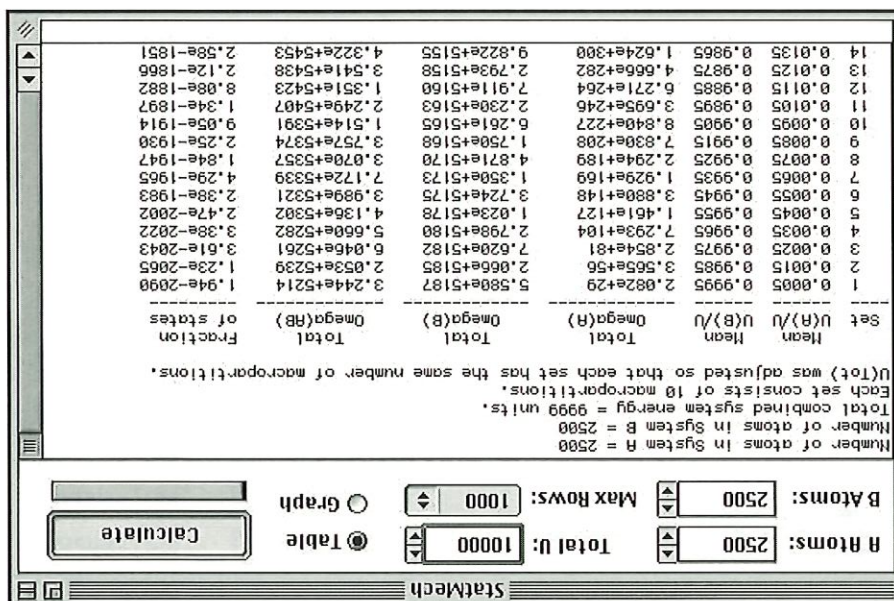


Figure T5.3

The macropartition table for a system 10 times larger than the one in figure T5.2. Note that the multiplicity exponents increase by about a factor of 10!

Note that even the probability of the system's remaining somewhere in the original set of macropartitions is negligible compared to the probability of its going on to the next set closer to equilibrium:

$$\frac{\text{Pr}(\text{no change})}{\text{Pr}(B \rightarrow A)} \approx \frac{\Omega_{AB}(U_A \approx 0.0125U)}{\Omega_{AB}(U_A \approx 0.0135U)} = \frac{3.5 \times 10^{5438}}{4.3 \times 10^{5453}} = 0.8 \times 10^{-15} \quad (\text{T5.4})$$

### Exercise T5X.3

Using StatMech, scale the system up by a factor of 10 again. (Note that a cubic solid containing 25,000 atoms is still only about 30 atoms on a side.) Show that the probability that the system will stay in the original set of macropartitions compared to going to the next set closer to equilibrium (the ratio analogous to the one shown in equation T5.4) is only  $0.5 \times 10^{-150}$ . What is the value of the ratio analogous to the one in equation T5.3?

When the numbers become as large as those shown in exercise T5X.3, the idea that the system could in principle stay in the same macropartition (or even move to a macropartition farther away from equilibrium) has no practical meaning: we will never, never, never, even if we watch for Avogadro's number of lifetimes of the universe, observe a system larger than 10,000 atoms do anything but inexorably march toward macropartitions where the energy is more evenly distributed between its subsystems.

The computer program Equilib (also available for free download from the *Six Ideas* website) illustrates this process in action. This program models two Einstein solids in thermal contact, each of which consists of 400 fundamental oscillators (about 133 atoms' worth) arranged in a  $20 \times 20$  grid of squares. Initially, the oscillators in system A have zero energy, while each oscillator in solid B has 5 units of energy. Each time step, the program scans through all 800 oscillators. If a given oscillator has any energy, the program either transfers 1 unit of energy to a randomly selected one of the oscillator's eight neighbors



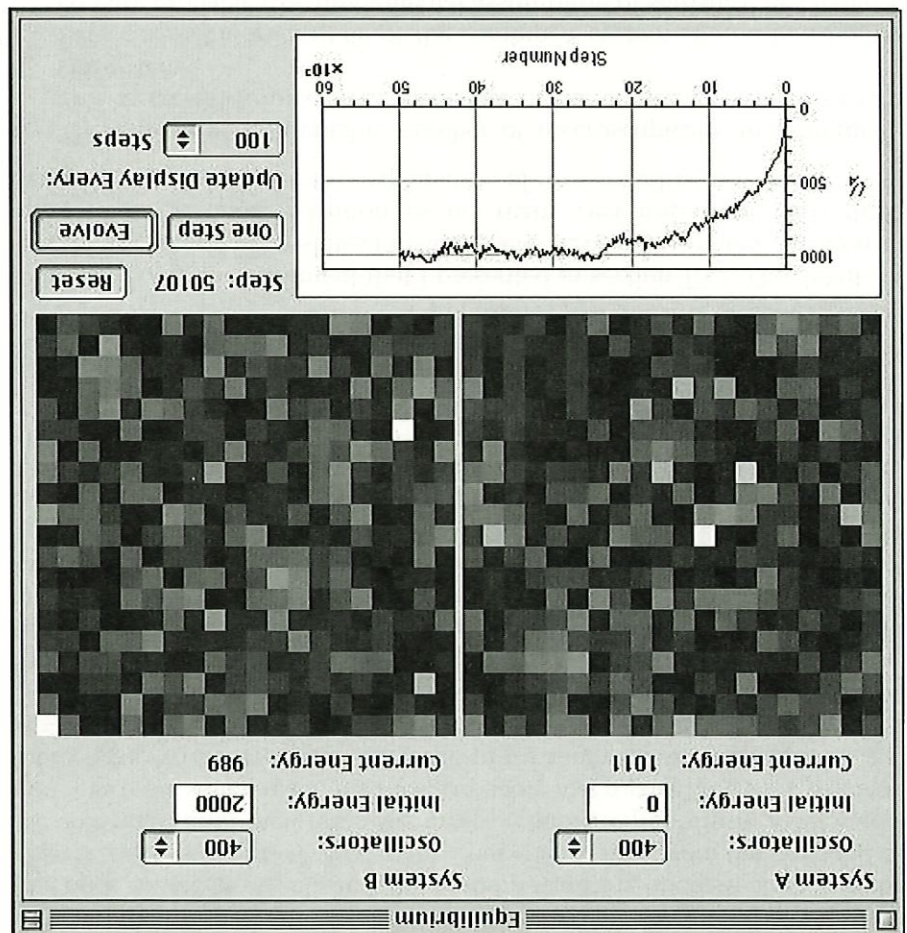


Figure T5.4

A screen shot of the Equilib program in action. Each small square represents an individual quantum oscillator that exchanges energy with its neighbors. Each square's brightness reflects the amount of energy in the corresponding oscillator.

or allows the oscillator to keep its energy (with equal probability for each of the nine possibilities). Note that solids A and B can interchange energy because oscillators along the right edge of solid A are neighbors to the oscillators along the left edge of solid B, and vice versa. After doing this for each oscillator, the program updates a display that shows each oscillator as a shaded square whose brightness indicates how many energy units the oscillator stores (see figure T5.4). The program also updates a graph showing the total energy in solid A as a function of the step number.

I strongly recommend that you play with this program; it is fascinating to watch. The point is that this program simulates a completely random interchange of energy between simple identical oscillators. It knows nothing about microstates or macrostates. Even so, you can see that (even for this very small system)  $U_A$  marches pretty much inexorably upward as time passes until the system reaches equilibrium at about step 25,000; thereafter,  $U_A$  fluctuates randomly about that most probable macropartition (where  $U_A = 1000\epsilon$ ). In other words, this simple system exhibits directly how random microscopic processes can lead to an essentially irreversible transfer of energy from a hot solid to a cold solid!

So, let us take a step back and consider what this means at the macroscopic level. I take a solid with a lot of thermal energy and place it in contact

with an otherwise identical solid with little thermal energy. What we see is that once contact is established, the random shuffling of energy between the objects leads with *virtual certainty* to a net energy flow from the hot solid to the cold solid until they reach the most probable (equilibrium) macropartition. Once the solids reach the most probable macropartition, they will stay there, again with virtual certainty, except for tiny random fluctuations (that are essentially immeasurable for large systems).

This, then, (at least in the context of Einstein solids) is the answer to the fundamental question of this unit. Why are some macroscopic processes irreversible? Specifically, why does heat always flow from hot to cold and never the other way? The answer is that *there are more microstates in that direction*. It is not because energy cannot *in principle* flow the other way. It is not because the time-reversible laws of microscopic physics for some reason do not apply here. Complex objects simply evolve by random process to the macrostates that contain the most microstates. It is really (surprisingly, wonderfully) simple!

### T5.3 Irreversibility in General

Look back over the argument that I presented in section T5.2. The details of exactly how many microstates Einstein solids have in this macropartition as opposed to that macropartition are not really very important. Only three things have to be true for this explanation of irreversibility to work:

1. There must be a countable number of macroscopically indistinguishable microstates for every macrostate of the combined system of two subsystems.
2. Each accessible microstate of the combined system should be roughly equally probable (the fundamental assumption of statistical mechanics).
3. Each subsystem's multiplicity must (like that of a large Einstein solid) be a *very* rapidly increasing function of its thermal energy  $U$ .

The first of these requirements is a simple consequence of quantum mechanics, which requires the energy states of any bound system to be quantized. So long as we can use quantum mechanics to describe the system (which we can for all systems as far as we know), the first statement will be true. The second is the fundamental *assumption* of our model, but predictions based on that assumption do seem to be correct in a very wide range of circumstances. So let us focus on answering the following questions about the third requirement: (1) why does irreversibility necessarily follow if it is true, and (2) is it true for most macroscopic objects?

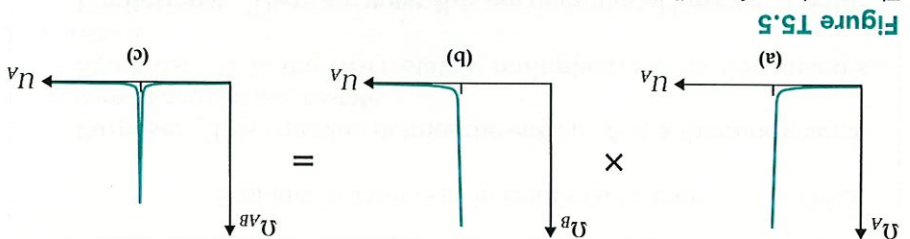
In any situation where the last statement is true, the combined system's multiplicity will exhibit an extremely sharp peak at the most probable macropartition. To see how this works, consider the graphs shown in figure T5.5. Imagine that we set the scale of the vertical axis of a graph so that the top of the scale corresponds to the value of subsystem  $A$ 's multiplicity  $\Omega_A$  at some arbitrarily chosen value  $U_0$  of its thermal energy. If  $\Omega_A$  increases rapidly with thermal energy, then at values of  $U_A$  greater than  $U_0$  it will be off the scale, and at values even a bit less than  $U_0$  it will be so much smaller as to be essentially zero. Therefore, a graph of  $\Omega_A$  versus  $U_A$  will look something like that shown in figure T5.5a. Moreover, if subsystem  $B$ 's multiplicity is a very rapidly increasing function of its internal energy  $U_B$ , then when system  $B$  is in contact with system  $A$ , its multiplicity will be a very rapidly *decreasing* function of  $U_A$  (since if  $U_A$  increases,  $U_B$  decreases). Therefore, a graph of  $\Omega_B$  versus  $U_A$  will look something like that shown in figure T5.5b. The combined system's

Why the third statement implies irreversibility

The general requirements for irreversible behavior



The product of rapidly increasing and rapidly decreasing functions is a spike. (In all three graphs, I have defined the vertical axis so that the value of the function at the mark on the horizontal axis is full scale on the graph's vertical axis.)



multiplicity, which is the product  $\Omega_{AB} = \Omega_A \Omega_B$  of these functions, will indeed be a sharply peaked function of  $U_{AB}$  as shown in figure T5.5c.

So, as long as both  $\Omega_A(U_A)$  and  $\Omega_B(U_B)$  are *very* rapidly increasing functions,  $\Omega_{AB}$  will increase so rapidly as one goes toward the peak and the numbers involved will be so huge that the probability that random processes happen to move the system *away* from the peak will be zero for all practical purposes. Moreover, the peak will be so narrow that once the combined system arrives at the vicinity of the peak macropartition, it will stay within a very narrow range with virtual certainty. Therefore, such a system will exhibit all the hallmarks of irreversible behavior.

We have seen that this statement is true for the Einstein solid, but is it true for other thermodynamic systems? It is indeed! I in fact chose the Einstein solid as our working example not only because it is relatively easy to count its microstates but also precisely because *its behavior in this regard is completely typical of the vast majority of complex systems.*

To predict *precisely* how rapidly the multiplicity of a substance increases with energy, we need to construct a detailed model of the substance, and doing this can be pretty difficult. But *qualitatively*, almost any macroscopic system behaves as an Einstein solid. Like an Einstein solid, any macroscopic system will contain a huge number of atoms or molecules, each of which can be in a variety of different energy states. The details of how a molecule's energy levels are spaced may be different, but (as long as there is no upper limit on the molecule's energy) such details do not affect the qualitative result that there will be a *huge* number of ways to distribute the system's energy among the molecules and that increasing the energy even a small amount opens up a vast number of new possibilities for distributing that energy. My point is that the argument presented in this chapter that explains the irreversible behavior of Einstein solids also *qualitatively* applies to essentially all other macroscopic systems as well.

## T5.4 The Definition of Entropy

To know which macropartitions of a combined system are the most probable, we need to know how many microstates the system has in that macropartition. However, as we have seen, the number of microstates available to even a tiny system can be so large as to be extremely awkward. Indeed, the number of microstates available to Einstein solids involving Avogadro's number of atoms are in the ballpark of  $10^{23}$  (that is, 1 followed by Avogadro's number of zeros). Such numbers are truly unmanageable. For realistically sized objects, we need a less awkward way to talk about multiplicity.

Toward this end, we define an object's **entropy**  $S$  in a given macrostate

The definition of entropy

$$S \text{ (of macrostate)} \equiv k_B \ln \Omega \text{ (of macrostate)} \quad (\text{T5.5})$$

**Purpose:** This equation defines the entropy  $S$  of a thermodynamic

system in a given macrostate.

**Symbols:**  $\Omega$  is the macrostate's multiplicity;  $k_B$  is Boltzmann's

constant.

**Limitations:** There are none; this is a definition. However, it is dif-

ficult to determine  $\Omega$  exactly in many situations.

Entropy of an Einstein solid

Some nice features of this definition

In the specific case of an Einstein solid, whose macrostate is specified by  $U$  and  $N$ , its entropy is a function of  $U$  and  $N$ :

$$S(U, N) \equiv k_B \ln \Omega(U, N) = k_B \ln \frac{(3N + U/\epsilon - 1)!}{(3N - 1)! (U/\epsilon)!} \quad (\text{T5.6})$$

Why this definition? Entropy is really just another way of talking about the *multiplicity*: when the multiplicity is large, the entropy is large. Defining the entropy in terms of the *natural logarithm* of the multiplicity, however, serves two very useful purposes. First, it makes the awkwardly large multiplicity values easier to manage. For example, the logarithm of a multiplicity  $\Omega = 10^{10^{23}}$  is about  $2.3 \times 10^{23}$ . While still a large number, this is much more manageable than the multiplicity itself.

Second, consider a specific macropartition of a system of two systems in thermal contact. The multiplicity of the combined system in this macropartition is  $\Omega_{AB} = \Omega_A \Omega_B$ , where  $\Omega_A$  and  $\Omega_B$  are the multiplicities of the individual systems in their specified macrostates. This implies that the total entropy of the combined system in that macropartition is conveniently the simple *sum* of the solids' individual entropies in that macrostate.

$$S_{AB} = S_A + S_B \quad (\text{T5.7})$$

**Purpose:** This equation describes the total entropy  $S_{AB}$  for a given

macropartition of a system consisting of two subsystems  $A$  and  $B$  in

thermal contact.

**Symbols:**  $S_A$  and  $S_B$  are the subsystems' entropies in that macro-

partition.

**Limitations:** There are none. This directly follows from the defini-

tions of entropy and multiplicity.

## Exercise T5X.4

Show that equation T5.7 follows from the definition of entropy and the mathematical fact that  $\ln xy = \ln x + \ln y$ .

We could have defined  $S = \ln \Omega$  without multiplying the logarithm by  $k_B$  (and a handful textbook authors do this). This shares all the advantages of the conventional definition and in a certain sense more fundamentally captures the essence of entropy. The constant  $k_B$  just rescales  $\ln \Omega$  in a way that we will see is helpful when we explore the definition of temperature in chapter T6. For now, simply note that since  $k_B = 1.38 \times 10^{-23} \text{ J/K}$ , a multiplicity on the order of magnitude of  $10^{10^{23}}$ , whose logarithm is about  $2.3 \times 10^{23}$ , will have a corresponding entropy  $S = k_B \ln \Omega$  of about  $4 \text{ J/K}$ , a number of convenient size.



## Example 15.1

**Problem** Imagine a situation in which we have two Einstein solids in thermal contact with  $N_A = N_B = 250$  and  $U = 1000\epsilon$ . (a) Find the entropies of both individual solids and the combined system in this macropartition where  $U_A = 12\epsilon$ . (b) Compare the entropy of the total system in this macropartition with that of the total system in the central macropartitions (where  $S_{AB} = 9.86 \times 10^{26}$ ). Express all entropies as a multiple of  $k_B$ .

**Translation** According to figure T5.2,  $S_A = 7.22 \times 10^{25}$ ,  $S_B = 1.03 \times 10^{514}$ , and  $S_{AB} = 7.42 \times 10^{539}$ .

**Model** The first of the entropies is easy to calculate directly:  $S_A \equiv k_B \ln \Omega_A = 59.5k_B$ . However, my calculator cannot handle exponents greater than 99, so I cannot calculate either  $\ln \Omega_B$  or  $\ln \Omega_{AB}$  directly. However, one of the properties of the natural logarithm is that  $\ln x^a = a \ln x$ , so  $\ln 10^{514} = 514 \ln 10 = 514(2.30258)$ . Moreover,  $\ln xy = \ln x + \ln y$ .

**Solution** Therefore,

$$\ln \Omega_B = \ln 1.03 + \ln 10^{514} = 0.030 + 514(2.30258) = 1183.56 \quad (\text{T5.8})$$

so  $S_B = 1183.56k_B$ . Similarly,  $S_{AB} = k_B [\ln 7.42 + 539(2.30258)] = 1243.10k_B$ . The entropy of the central macropartitions is  $S_{AB} = k_B [\ln 9.86 + 726(2.30258)] = 1673.97k_B$ .

**Evaluation** This is substantially larger, as expected.

## Example 15.2

**Problem** Imagine that one macropartition of a combined system of two Einstein solids has an entropy of  $S_1 = 432.5k_B$ , while another (where the energy is more evenly divided) has an entropy of  $S_2 = 546.3k_B$ . How many times more likely is it that you will find the system in the second macropartition than in the first?

**Model** The probability of a given macropartition being observed is proportional to its multiplicity  $\Omega$ . Now, the natural log and exponential functions are inverses, so  $e^{\ln x} = x$ . Since the definition of entropy is  $S = k_B \ln \Omega$ , this means that  $\Omega = e^{S/k_B}$ .

**Solution** Therefore, the ratio of the probabilities in this case is

$$\frac{\Omega_2}{\Omega_1} = \frac{e^{S_2/k_B}}{e^{S_1/k_B}} = \frac{e^{546.3}}{e^{432.5}} = e^{546.3-432.5} = e^{113.8} = 2.6 \times 10^{49} \quad (\text{T5.9})$$

Therefore, we are  $2.6 \times 10^{49}$  times more likely to find it in the second macropartition than in the first macropartition.

## T5.5 The Second Law of Thermodynamics

We have seen that a system of two objects will evolve from macropartitions with lower multiplicities (and thus lower entropy) to macropartitions with higher multiplicities (higher entropy). Moreover, once the system reaches the macropartition having the highest multiplicity (highest entropy), it will stay there. For very tiny systems, these are merely statements of probability, but

The second law of thermodynamics

This law is one of the most important and useful laws of physics and is (as the British writer C. P. Snow once asserted) one of those things a well-educated person ought to know. It expresses in a precise and quantitative way the fact of irreversibility and has a number of important implications and applications that we will study in future chapters. But we should never lose sight of the fact (as Boltzmann first argued) that this great law is a consequence of the more fundamental ideas presented in section T5.3.

*The entropy of an isolated system never decreases.*

**second law of thermodynamics**, expresses the essence of this idea: T5.8 for a numerical example). The following simple law, known as the entropy is measurably smaller is extraordinarily improbable (see problem cause the idea that the system would evolve to a macropartition where its entropy of a (sufficiently large) system will never be observed to decrease, be- ties to those with larger multiplicities, *its entropy inevitably increases*. The a large system inevitably evolves from macropartitions with low multiplici- plicities turn probabilities in principle to certainties in practice. Therefore, as for anything approaching a normal-size system, the extremely large multi-

Examples of disorder linked to multiplicity

## T5.6 Entropy and Disorder

Many popular treatments link *entropy* to the concept of *disorder*. Here we have defined entropy in terms of *multiplicity*. How are these ideas related?

Think about it this way. Why does your dorm room get disorderly unless you specifically clean it up? Because that's where the microstates are. There are many, many more ways for your room to be disorderly than orderly. Because of this, random things that happen in your room are far more likely to contribute to disorder than to greater order. (What is the likelihood that an earthquake will pick up your clothes and hang them back up in your closet?)

Let us consider some more physical examples of disorder. A flowing liquid of a certain kind of atom has greater disorder than a neat crystalline solid made of the same atoms. A substance with a sufficient amount of thermal energy will therefore be a liquid instead of a solid because that's where the microstates are: there are many, many more microstates available to molecules if they are free to roam around than if they are confined to a solid.

Figure T5.6 shows a container with two compartments. Before mixing, each compartment contains different gases. A valve between the two compartments is then opened, allowing the gases to mix with each other. You may know that under such circumstances, the gases will spontaneously intermingle, just as a drop of cream put in a cup of coffee will naturally diffuse throughout the cup (although a little stirring speeds up the process). Why do the gases spontaneously mix, becoming more "disorderly" in a certain sense? Because that's where the microstates are. There are many, many, many more

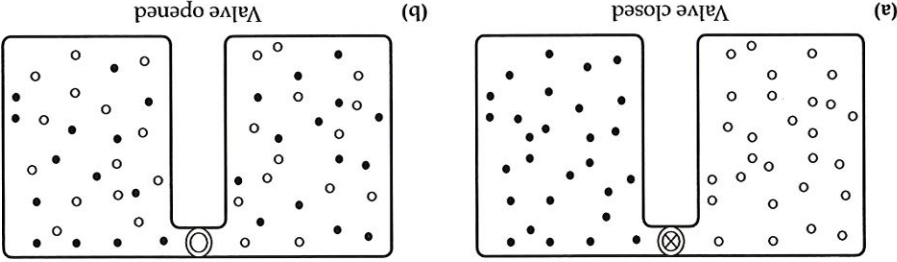
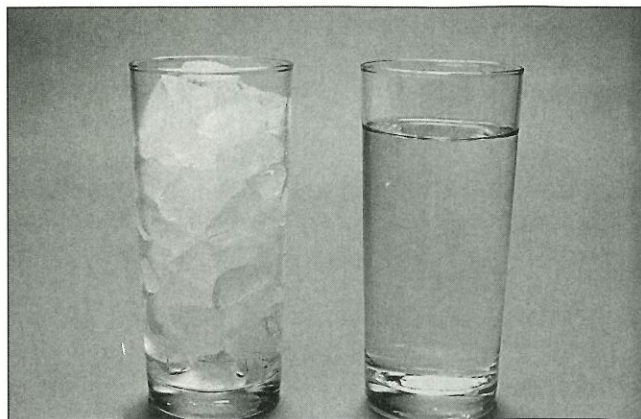


Figure T5.6

Spontaneous mixing of gases.





**Figure T5.7**

The contents of which glass have the higher entropy?

microstates available to the system when the gas molecules are free to roam over the entire container than there are when the gases are separated and confined to their side of the valve.

So in many standard situations, increased multiplicity is indeed linked with disorder. It is important to remember, however, that entropy is defined in terms of *multiplicity*, not disorder. Increasing entropy does not *necessarily* imply increasing disorder (at least *visible* disorder).

For example, consider the glass of crushed ice and the glass of water shown in figure T5.7. Which of the two glasses has a higher entropy? The crushed ice may *look* more disorderly; but since we have to add energy to the ice to convert it to water, and since the multiplicity of virtually all macroscopic systems increases dramatically when we add energy, the multiplicity (and thus the entropy) of the nice, orderly glass of water is much larger.

Another potentially confusing example is life itself. Life has been described by some as being anti-entropic, because living things take unorganized inorganic matter and transform it to the most intricate and complex order that one can imagine. Is this not inconsistent with the law of increasing entropy?

Not at all! No creature is an isolated system. In fact, every creature releases energy into its environment as it organizes matter. This energy causes the entropy of the creature's surroundings to increase far more than the creature decreases its own entropy by putting a few things in order. Indeed, thoughts in a brain, movements of a muscle, growth, development, even evolution itself should be considered examples of *entropy in action*. Sources of energy are tapped by living things and ultimately dissipated into the environment, and this natural, spontaneous flow of energy from being concentrated to dissipated is cleverly tapped by organisms to help accomplish a little organization along the way. The beautiful order of life is thus a *manifestation* of the dissipation of energy (and consequent increase in entropy of the universe) in much the same way as the orderly ticking of a clock manifests the winding down of its spring. Stars and galaxies form, the sun shines, tectonic plates move, volcanoes erupt, storms form, and flowers bloom in the spring because all systems in the universe are evolving toward the macropartitions that maximize their entropy (see figure T5.8). Every physical process in our daily life, whether associated with growth or decay, increasing order or increasing disorder, is not merely *consistent* with the second law of thermodynamics: it is a *consequence* of that law.

There are some cases, then, in which the idea of *entropy as disorder* can be misleading. Whenever there appears to you to be a contradiction between the concepts of entropy as disorder and entropy as multiplicity, you should remember that *multiplicity* is the more basic concept.

In some cases, the link with disorder is misleading

The basic meaning of entropy is multiplicity, *not* disorder





**Figure T5.8**  
Entropy in action (the flowers, too).

## TWO-MINUTE PROBLEMS

- T5T.1** A hot object is placed in contact with a cold object. Heat is observed to flow spontaneously from the hot object to the cold object, but not in the other direction. According to the argument in this chapter, this is so because
- This increases the entropies of both objects.
  - This decreases the entropy of the combined system.
  - The system will tend to evolve toward macropartitions that have more microstates.
  - A and C
  - B and C
- T5T.2** Consider a system whose multiplicity is always 1, no matter how much energy you put into it. If you put a very large amount of energy into such an object (object A), and place it into thermal contact with an Einstein solid (object B) having the same number of atoms but much less energy, what will happen?
- Energy flows from A to B until A has virtually no energy.
  - Energy flows from B to A until B has virtually no energy.
  - Energy flows from A to B until they have the same energy.
  - No energy will flow between A and B at all.
  - Something else happens (describe).
- T5T.3** Consider a system comprised of two or more objects in contact. The system's total entropy in a given macropartition is always equal to the *sum* of the entropies of its parts (T or F).
- T5T.4**  $10^{62}/10^{60} = 100$ . What is  $\ln 10^{62}/\ln 10^{60}$ ? (Select the closest response.)
- 100
  - 10
  - 4.6
  - 1.0
- T5T.5** The entropy of a certain macropartition of a combined system is  $102k_B$ . The entropy of another macropartition is  $204k_B$ . How much more likely is the system to be in the second macropartition than the first? (Select the closest response.)
- 2 times
  - $e^2 = 7.4$  times
  - $10^2 = 100$  times
  - $e^{102} = 2 \times 10^{44}$  times
  - $e^{102k_B} \approx e^0$ ; the two macropartitions have basically the same probability
- T5T.6** Which system has the greater entropy, a puddle of water sitting on a table next to a chaotic scattering



- of salt crystals or the same amount of salt dissolved in an evenly distributed way in the puddle? Be prepared to describe your reasoning.
- A. The puddle and the scattered crystals.
- B. The puddle with the dissolved salt.
- C. Both have the same entropy.
- D. There is no way to tell without having detailed models of both the water and the salt.

## HOMEWORK PROBLEMS

### Basic Skills

**T5B.1** Consider the system consisting of a pair of Einstein solids in thermal contact. A certain macropartition has a multiplicity of  $3.7 \times 10^{1024}$ , while the total number of microstates available to the system in all macropartitions is  $5.9 \times 10^{1042}$ . If we look at the system at a given instant of time, what is the probability that we will find it to be in our certain macropartition?

**T5B.2** Consider the system consisting of a pair of Einstein solids in thermal contact. A certain macropartition has a multiplicity of  $1.2 \times 10^{346}$ , while the total number of microstates available to the system in all macropartitions is  $5.9 \times 10^{362}$ . If we look at the system at a given instant of time, what is the probability that we will find it to be in our certain macropartition?

**T5B.3** Consider the system consisting of a pair of Einstein solids in thermal contact. Imagine that it is initially in a macropartition that has a multiplicity of  $8.8 \times 10^{123}$ . The adjacent macropartition closer to the equilibrium macropartition has a multiplicity of  $4.2 \times 10^{134}$ . If we look at the system a short time later, how many times more likely is it to have moved to the second macropartition than to have stayed with the first?

**T5B.4** Consider the system consisting of a pair of Einstein solids in thermal contact. Imagine that it is initially in a macropartition that has a multiplicity of  $7.6 \times 10^{3235}$ . The adjacent macropartition closer to the equilibrium macropartition has a multiplicity of  $4.1 \times 10^{3228}$ . If we look at the system a short time later, how many times more likely is it to have moved to the second macropartition than to have stayed with the first?

**T5B.5** An Einstein solid in a certain macrostate has a multiplicity of  $3.8 \times 10^{280}$ . What is its entropy (expressed as a multiple of  $k_B$ )?

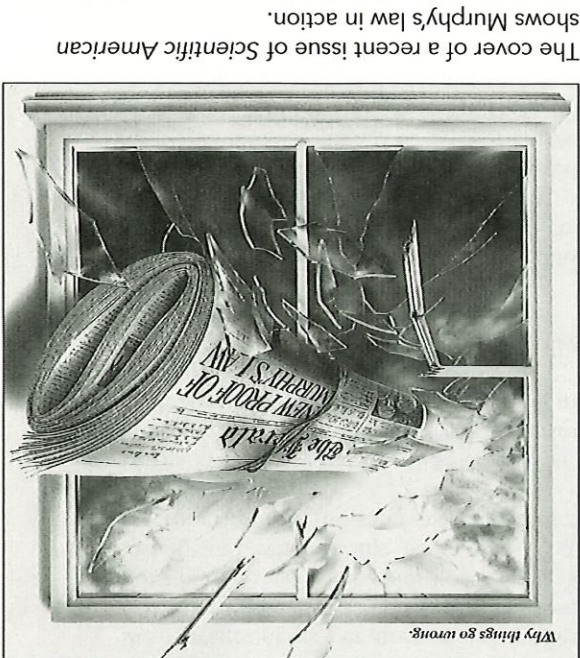
**T5B.6** A pair of Einstein solids in a certain macropartition has multiplicities of  $4.2 \times 10^{320}$  and  $8.6 \times 10^{132}$ . What are the entropies of each solid? What is the total entropy of the system in this macropartition? (Express entropies as multiples of  $k_B$ .)

**T5B.7** Is it *really* true that the entropy of an isolated system consisting of two Einstein solids *never* decreases? (Consider a pair of very small solids.) Why is this statement more accurate for large systems than for small systems? Explain in your own words.

### Synthetic

**T5S.1** You ask your roommate to clean up a mess he or she made in your room. Your roommate refuses, because cleaning up the mess would violate the second law of thermodynamics, and campus security's record of your roommate's legal violations is already excessive. Gently but firmly explain why complying will not put your roommate at risk of such an infraction.

**T5S.2** The classic statement of Murphy's law reads, "If something can go wrong, it will." Explain how this is really a consequence of the second law of thermodynamics. (Hint: What is the entropy of "wrong" in a given context compared to the entropy of "right"?)



**T5S.3** (a) Run the StatMech program for two Einstein solids in contact with  $N_A = N_B = 100$  and  $U = 200\epsilon$  and answer the following questions. (1) How many times more likely is the system to be found in the center macropartition than in the extreme macropartition where  $U_A = 0$  and  $U_B = 200\epsilon$ ? (2) What is the range of values that  $U_A$  is likely to have more than 99.98% of the time? (3) If  $U_A$  were initially to have the extreme value 0, how many times more likely is it to move to the next macropartition nearer the center than to remain in the extreme one?



Use these techniques to solve the following problem. The entropy of the most probable macropartition for a certain system of Einstein solids is  $6025.3k_B$ , while the entropy of an extreme macropartition is only  $5755.4k_B$ . What is the probability of finding the system at a given time in the extreme macropartition compared to that of finding it in the most probable macropartition?

## T5S.8

*In principle*, the entropy of an isolated system decreases a little bit whenever random processes cause its macropartition to fluctuate away from the most probable macropartition. We can certainly see this with small systems (see figure T5.4). But is this really a possibility for a typical macroscopic system? Imagine that we can measure the entropy of a system of two solids to within 2 parts in 1 billion. This means that we could just barely distinguish a system that has an entropy of  $4.999999999 \text{ J/K}$  (eight 9s) from one that has  $5.000000000 \text{ J/K}$ . (This is a reasonable entropy for a macroscopic system.)

(a) Imagine that the entropy of the equilibrium macropartition is  $5.000000000 \text{ J/K}$ . Show that the approximate probability that at any given time later we will find the system in a macropartition with entropy  $4.999999999 \text{ J/K}$  (i.e., with an entropy that is only barely measurably smaller) is about  $10^{315,000,000,000,000}$  times smaller than the probability we will still find it to have entropy  $5.000000000 \text{ J/K}$ . (*Hint*: See problem T5S.7.)

(b) Defend the statement that the entropy of an isolated system in thermal equilibrium *never* decreases.

## Rich-Context

## T5R.1

According to a reputable checkout-counter news source, space aliens give top scientists an object made of a substance that can store thermal energy but whose multiplicity actually *decreases* as its energy increases. What will happen to such an object if it is placed in thermal contact with a normal object (such as an Einstein solid)? Can this object ever be in thermal equilibrium with a normal object? If you put an object of this substance in a flame, will the flame warm it? How might you increase the thermal energy of such an object? Do you think that we can assign a meaningful temperature to such an object? Answer these questions *qualitatively*, but carefully, supporting your answers with arguments based on the ideas in this chapter. (*Hint*: What would a macropartition table look like for such an object in contact with an Einstein solid?)

*Comment*: This is not just a science fiction scenario: certain real physical systems can exhibit such behavior. For example, if one sets up the system described in problem T4R.1 with enough initial energy in a very low-temperature environment, it can behave in this way. In general, this kind of weird behavior is possible in systems where there is an upper limit on the energy that a molecule can hold, which is not the case in Einstein solids and most other substances.

## T5S.4

Consider two Einstein solids in thermal contact. The solids have different values of  $N$  but are identical in all other respects. It is *plausible*, since every atom in the combined system is identical, that in equilibrium the energy will be distributed among the solids in such a way that the average energy per atom is the same. Use StatMech to test this hypothesis in the situation where  $U = 1000\epsilon$  and  $N_A$  and  $N_B$  have various different values such that  $N_A + N_B = 1000$ . (Set Max Rows to 1000 so that you can see every macropartition.)

(a) Is it true in *most* cases that in the most probable macropartition the solids have energies such that the average energy per atom in each is the same? Is it strictly true in *every* case? Answer these questions by discussing the values of  $N_A$  and  $N_B$  you tested, and whether the actual most probable macropartition is the same as that predicted by the hypothesis.

(b) In any case where the hypothesis does *not* work, does increasing both  $N_A$  and  $N_B$  by a factor of 10 or 100 (but leaving  $U$  alone) yield a result more or less consistent with the hypothesis?

(c) Speculate as to the value of this hypothesis in the large- $N$  limit.

## T5S.5

(a) What is the entropy of an Einstein solid with 5 atoms and an energy of  $15\epsilon$ ? Express your answer as a multiple of  $k_B$ .

(b) What is the entropy of an Einstein solid with 50 atoms and an energy of  $100\epsilon$ ? Express your answer as a multiple of  $k_B$ . (*Hint*: You will find that using StatMech is by far the fastest way to calculate the multiplicity here.)

## T5S.6

A certain macropartition of two Einstein solids has an entropy of  $305.2k_B$ . The next macropartition closer to the most probable one has an entropy of  $335.5k_B$ . If we check it again later, how many times more likely is it to have moved to the other than to have stayed in the first?

## T5S.7

My calculator cannot display  $e^x$  for  $x > 230$ . One can calculate  $e^x$  for larger values of  $x$  as follows. Define  $y$  such that  $x \equiv y \ln 10$ . This means that  $e^x = e^{y \ln 10} = (e^{\ln 10})^y = 10^{y \ln 10}$ . Note that we can calculate  $10$  raised to a non-integer power (for example,  $10^{3.46}$ ) as follows:  $10^{3.46} = 10^{3+0.46} = 10^3(10^{0.46}) = 10^3 \times 10^3$ .



T5R.2 (Adapted from Kittel and Kroemer, *Thermal Physics*,

2d ed., p. 53.) The writer Aldous Huxley is reported to have said that "six monkeys, set to strum unintelligently on typewriters for millions of years would be bound in time to write all of the books in the British Museum." This statement is in fact completely false: Huxley has been misled by an incorrect intuition about the character of extremely large numbers.

Let us set ourselves a much less challenging task. Imagine that we have 10 billion monkeys (somewhat more than the human population of the earth) typing diligently at the rate of 2 characters per second since the universe began  $5 \times 10^{17}$  s ago. Instead of requiring an entire library, we will settle for a single typed version of *Hamlet*. Let us guess that *Hamlet* has approximately  $10^5$  characters.

(a) Assume that the typewriters used by the monkeys have 26 letters and 10 punctuation characters (space, carriage return, period, comma, colon, semicolon, quotation mark, apostrophe, dash, question mark) for a total of 36 characters. We will ignore the distinction between capital letters and small letters. The probability that any given character is the first character in *Hamlet* is thus  $1/36$ . The probability that this character and the next are the first two characters of *Hamlet* is  $(1/36)(1/36) = (1/36)^2$ . Argue, then, that the probability that any given sequence of  $10^5$  random characters is *Hamlet* is  $10^{-155.630}$ . (Hint:  $\log x^n = n \log x$ , where  $\log$  is the base-10 logarithm.)

(b) Argue that the probability that *Hamlet* would be randomly typed by any of our army of monkeys since the beginning of the universe is about  $10^{-155.602}$ . (Hint: Remember that any key typed by any monkey could in principle be the first character in the play.) This probability is zero in any practical sense: Even our huge bevy of monkeys will never, never, never be able to type *Hamlet* at random.

## ANSWERS TO EXERCISES

T5X.1 The probability of the 1:199 macropartition is  $3.3 \times 10^{-41}$ .

T5X.2 The number of seconds since the beginning of the universe is very roughly  $(1.4 \times 10^{10} \text{ y})(3 \times 10^7 \text{ s/y}) = 4 \times 10^{17}$  s. If we peek 1 billion times per second, we will have peeked about  $(4 \times 10^{17})(10^9) = 4 \times 10^{26}$  times since the beginning of the universe. Since the probability that any peek yields  $U_A = 0$  is roughly  $4 \times 10^{-43}$ , the probability that we will have seen this value of  $U_A$  in any one of our peeks is roughly  $(4 \times 10^{-43})(4 \times 10^{26}) \approx 2 \times 10^{-16}$ . This is a small enough probability that I would be willing to bet my life on this not happening.

T5X.3 The probability of  $U_A$  moving  $0.001U$  from  $U_A = 0.0125U$  toward smaller energy as opposed to larger energy in this case is

## Advanced

T5A.1 We can estimate the approximate size of a system's fluctuations around the equilibrium macropartition as follows. When the number of molecules  $N$  is extremely large, many substances have multiplicities of the form  $\Omega \approx C U^a N^b$ , where  $U$  is the substance's thermal energy,  $C$  is a quantity that depends on the type of substance and  $N$  but not on  $U$ , and  $a$  is a substance-dependent constant of the order of magnitude of 1. Imagine two identical objects in thermal contact. a. Argue that we can write the multiplicity of a combined system with total energy  $U$  as

$$\Omega_{AB} \approx B(1 - x^2)^{aN} \quad \text{where } x \equiv \frac{U_A - \frac{1}{2}U}{U_A - \frac{1}{2}U} \quad \text{(T5.10)}$$

and  $B$  is another quantity that does not depend on  $U$ . Note that the variable  $x$  here specifies how far we are from equilibrium. If  $x = 0$ , then  $U_A = \frac{1}{2}U$ , which is the equilibrium macropartition, and  $x = \pm 1$  corresponds to the extreme macropartitions  $U_A = U$  and  $U_A = 0$ , respectively. Note that  $\Omega_{AB}$  has a peak at  $x = 0$  and falls off very rapidly as the absolute value of  $x$  grows.

b. Show the value of  $x$  where  $\Omega_{AB}$  has fallen to one-half of its peak value is

$$x_{1/2} = \pm \frac{1}{\sqrt{2aN}} \quad \text{(T5.11)}$$

(Hint: Argue that one can use the binomial approximation to calculate the binomial.) Assuming that  $a \approx 1$  and  $N \approx 10^{24}$ , estimate very roughly how far a typical fluctuation will carry the energy of either system away from its equilibrium value  $\frac{1}{2}U$ , expressed as a fraction of that equilibrium value.

T5X.4 The multiplicity of any given macropartition of the combined system is

$$\Omega_{AB} = \Omega_A \Omega_B \quad \text{(T5.13)}$$

If we take the natural log of both sides, we get

$$\ln \Omega_{AB} = \ln \Omega_A \Omega_B = \ln \Omega_A + \ln \Omega_B \quad \text{(T5.14)}$$

Multiplying both sides of this equation by  $k_B$  and using the definition of  $S$  given by equation T5.5, we get equation T5.7.



# Temperature and Entropy

## T6

### Chapter Overview

#### Introduction

In this chapter, we will use the concepts presented in chapter T5 to develop a new and more fundamental definition of temperature that does not depend on the arbitrary choice of a practical thermometer. We will spend much of the rest of the unit exploring the practical implications of this definition.

#### Section T6.1: The Definition of Temperature

The total entropy  $S_{\text{TOT}} = S_A + S_B$  of a system consisting of two objects A and B is a maximum (by definition) when the system is in its equilibrium (most probable) macropartition. This means that in equilibrium

$$0 = \frac{dS_{\text{TOT}}}{dU_A} = \frac{dS_A}{dU_A} + \frac{dS_B}{dU_A} = \frac{dS_A}{dU_A} - \frac{dS_B}{dU_B} \Rightarrow \frac{dS_A}{dU_A} = \frac{dS_B}{dU_B} \quad (\text{T6.3})$$

(The next-to-last step follows because any energy that object A gains comes at the expense of object B, implying that  $dU_A = -dU_B$ .) By the zeroth law, the two objects' temperatures (by definition) must be equal in that macropartition as well. The mathematical consequence of these statements (as discussed in the section) is that the derivative  $dS/dU$  of an object's entropy  $S$  with respect to its thermal energy  $U$  must be equal to some function  $f(T)$  of that object's temperature  $T$ . The function  $1/T$  is the simplest choice for  $f(T)$  consistent with the idea that heat spontaneously flows from an object with a large value of  $T$  to an object with a lower value of  $T$ . Therefore we define an object's temperature as follows:

$$\frac{1}{T} \equiv \frac{dS}{dU} \quad (\text{when } V, N, \text{ etc. are constant}) \equiv \frac{\partial S}{\partial U} \quad (\text{T6.6})$$

**Purpose:** This equation defines an object's absolute temperature  $T$  in terms of the rate at which the object's entropy  $S$  increases with its internal energy  $U$ . **Limitations:** The derivative must be evaluated while holding all of the object's other macroscopic variables fixed (this is what the partial derivative symbol  $\partial S/\partial U$  means).

Note that since in principle we can calculate an object's multiplicity and thus its entropy if we have a decent model, we can calculate an object's temperature from fundamental principles without referring to a standard thermometer.

#### Section T6.2: Consistency with the Old Definition

Is this new definition of temperature at least approximately consistent with the old gas thermometer definition? We saw in chapter T2 that at sufficiently high temperatures, the thermal energy  $U$  of a monatomic solid satisfies the relationship  $U \approx 3Nk_B T$ ,

▷ Fundamentals of Thermal Physics	▷ The Meaning of Entropy	Macrostates and Microstates	The Second Law	Temperature and Entropy	▷ Applications and Applications
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where  $T$  in this equation was the old gas thermometer temperature. A calculation based on equation T6.6 yields the same result, strongly suggesting that the new definition of temperature is at least approximately the same as the old definition.

### Section T6.3: A Financial Analogy

Objects in thermal contact behave as people involved in financial transactions do if we say that

Energy	↔	Money
Entropy	↔	Happiness
Temperature	↔	Generosity

and assume that financial transactions between people always serve to increase the happiness of everyone involved. Just as the general happiness increases if money flows from a more generous person to a less generous person, the entropy of a thermodynamic system increases if energy flows from a high-temperature object to a lower-temperature one.

Most normal objects have entropies and temperatures that increase with energy, just as normal people's happiness and generosity increase when they receive money. It is possible to find physical systems that are "miserly" (whose temperature decreases as their energy increases) or "enlightened" (whose entropy increases as their energy decreases). The financial analogy helps us think clearly about how such exotic objects might behave when interacting with normal objects.

### Section T6.4: The Boltzmann Factor

We define a (thermal) reservoir to be an object so large that it can provide or absorb any energy likely to be exchanged in a situation of interest without undergoing a significant change in its temperature. Consider a small quantum system in thermal contact with such a reservoir. The probability that the quantum system will be in a quantum state with energy  $E$  is proportional to the multiplicity of the combined system. But the multiplicity of the quantum system in a given quantum state is 1 by definition, so the multiplicity of the combined system is the same as the reservoir's multiplicity. The reservoir's multiplicity will decrease as  $E$  increases because the quantum system's energy comes at the expense of the reservoir's energy. A short calculation involving the definition of temperature implies that the reservoir's multiplicity (and thus the state's probability) in fact decreases exponentially with  $E$ :

$$\text{Pr}(E) = \frac{1}{Z} e^{-E/k_B T} = \frac{\sum_{\text{all states}} e^{-E_i/k_B T}}{e^{-E/k_B T}} \quad (\text{T6.23})$$

**Purpose:** This equation describes the probability that a small system in thermal contact with a reservoir at absolute temperature  $T$  will be in a quantum state (i.e., a microstate) with energy  $E$ .  
**Symbols:**  $E_i$  is the energy of the  $i$ th quantum state of the small system,  $Z$  is a constant of proportionality, and  $k_B$  is Boltzmann's constant.  
**Limitations:** The reservoir must be large enough that it can provide the small system with any energy it is likely to have without suffering a significant change in its temperature  $T$ .  
**Note:** We call  $e^{-E/k_B T}$  the Boltzmann factor.

### Section T6.5: Some Simple Applications

Equation T6.23 has a large number of useful applications. This section illustrates how we can use the equation to calculate the probabilities of the two different configurations of a certain molecule in a solution at room temperature, and the probability that a hydrogen atom's electron will be in its first excited state at room temperature.

## T6.1 The Definition of Temperature

I stated in chapter T1 that statistical mechanics makes it possible to define absolute temperature in a very fundamental and general way *without* referring to any particular thermometer. My goal in this section is to present this new and powerful definition of temperature.

Consider again our famous *paradigmatic thermal process*, as illustrated in figure T6.1. A hot object is brought into contact with a cold object. Subsequently heat flows from the hot object to the cold object, decreasing the energy (and thus entropy) of the hot object and increasing the energy (and thus entropy) of the cold object.

Assuming that the two objects have a large number of molecules, the combined system will evolve inexorably toward the most probable macro-partition and subsequently remain there, in *thermal equilibrium*. The thermal equilibrium macropartition will therefore be the macropartition with the greatest number of microstates, and therefore the greatest total entropy

$$S_{\text{TOT}} = S_A + S_B.$$

Now, the combined system's entropy  $S_{\text{TOT}}$  is a function of the system's macropartition, which in a pure heat transfer process (where the volume  $V$ , the number of molecules  $N$ , and other macroscopic characteristics of the interacting objects are held constant) is completely determined by the objects' energies  $U_A$  and  $U_B$ . Actually, we only need to know  $U_A$  to determine the macropartition, since  $U_B = U - U_A$ , where  $U$  is the fixed total energy of the combined system. The macropartition where  $S_{\text{TOT}}$  is maximum is specified by the value of  $U_A$  such that

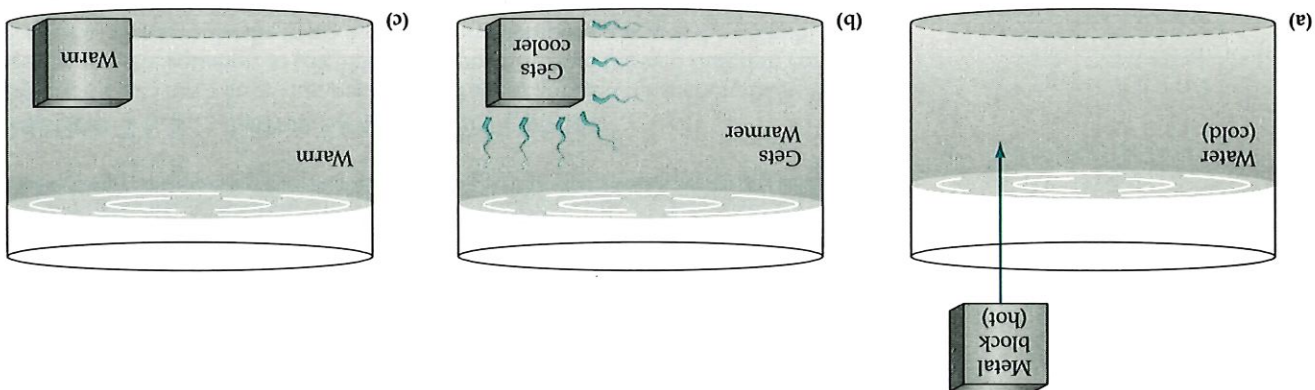
$$(T6.1a) \quad 0 = \frac{dS_{\text{TOT}}}{dU_A}.$$

(This is the usual way of finding the maximum of a function.) Since the system's total entropy  $S_{\text{TOT}} = S_A + S_B$ , we can rewrite this as follows:

$$(T6.1b) \quad 0 = \frac{d(S_A + S_B)}{dU_A} = \frac{dS_A}{dU_A} + \frac{dS_B}{dU_A}$$

by the sum rule of differential calculus. Now, according to the chain rule,

$$(T6.2) \quad \frac{dS_B}{dU_A} = \frac{dS_B}{dU_B} \frac{dU_B}{dU_A} = \frac{dS_B}{dU_B} (-1) = -\frac{dS_B}{dU_B}$$



**Figure T6.1**

The paradigmatic thermal process.



since  $U_B = U - U_A$ . (If you prefer a more informal argument, note that since any thermal energy gained by A is lost by B,  $dU_A = -dU_B$ . Plugging this into  $dS_B/dU_A$  yields  $-dS_B/dU_B$ .) If we plug equation T6.2 into equation T6.1b and rearrange things a bit, we find that the two objects will be in thermal equilibrium if and only if

$$\frac{dS_A}{dU_A} = \frac{dS_B}{dU_B} \quad (\text{T6.3})$$

The necessary condition for equilibrium

This is illustrated in figure T6.2.

### Exercise T6X.1

Verify equation T6.3.

Note that we can calculate the quantities on either side of equation T6.3 without reference to the other object: we simply take the derivative of an object's entropy  $S$  with respect to its own thermal energy  $U$  (holding its other macroscopic properties constant). This equation thus tells us that when two objects are in the equilibrium macropartition, the quantity  $dS/dU$  calculated for each object must be the same.

But the fundamental meaning of temperature (as the zeroth law of thermodynamics asserts) is that the temperature of two objects is the same in equilibrium. Therefore, the quantities  $dS/dU$  and temperature  $T$  must be linked in some one-to-one relationship. The most general way to describe this relationship is to say that for a given object

$$f(T) \equiv \frac{dS}{dU} \quad (\text{T6.4})$$

where  $f(T)$  is some as yet unknown function of the object's temperature  $T$ . Different choices for  $f(T)$  simply amount to different ways of linking  $dS/dU$  (the quantity most directly connected to equilibrium) to numerical temperature values. *In principle*, we could choose  $f(T)$  to be anything we like as long as  $f(T)$  has a unique value for every value of  $T$  (so that two objects having the same temperature necessarily have the same value of  $dS/dU$  and vice versa): our choice would simply define a new temperature scale. *In practice*, though, physicists elected to choose  $f(T)$  so that the new scale we define using equation T6.4 corresponds at least reasonably closely to the historical constant-volume gas thermometer scale described in chapter T1.

One desirable feature of that original scale is that heat flows from a hot object (i.e., one with a large value of  $T$ ) to a cold object (one with a low  $T$ ). As we have seen, energy flows spontaneously between two objects A and B in thermal contact because this allows the combined system's total entropy  $S_{\text{TOT}}$  to increase. Imagine that object A is the cold object, so that in an infinitesimal heat transfer process it gets a positive increment in energy  $dU_A$  from the other object. Since  $S_{\text{TOT}}$  must increase in this process,  $dS_{\text{TOT}}/dU_A$  must also be positive. Therefore, we have

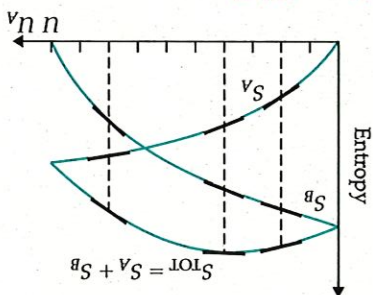
$$0 < \frac{dS_{\text{TOT}}}{dU_A} = \frac{dS_A}{dU_A} + \frac{dS_B}{dU_A} = \frac{dS_A}{dU_A} - \frac{dS_B}{dU_B} = f(T_A) - f(T_B) \quad (\text{T6.5})$$

Explain the reasoning behind each step in the sequence of equalities in equation T6.5.

### Exercise T6X.2

The system's total entropy is maximum where the slopes of the entropy curves for parts A and B become equal in magnitude and opposite in sign (at about  $U_A = 0.4U$  in the case shown). When this is so, the entropy gained by A when it gets a bit of energy  $dU_A$  from B is exactly balanced by the entropy lost by B. If the slopes are not equal, the system can gain entropy by transferring energy from one part to the other.

Figure T6.2



So for heat to flow from  $B$  to  $A$ , we must have  $f(T_A) > f(T_B)$ . But since object  $A$  here is the *cold* object, we see that as  $T$  increases, the value of  $f(T)$  should get *smaller*. The *simplest* definition of  $f(T)$  consistent with this requirement is  $f(T) = 1/T$ . So (following Boltzmann) we define temperature  $T$  as follows:

The fundamental definition of temperature

$$\frac{1}{T} \equiv \frac{dS}{dU} \quad (\text{when } V, N, \text{ etc. are constant}) \equiv \frac{\partial U}{\partial S} \quad (\text{T6.6})$$

**Purpose:** This equation defines an object's absolute temperature  $T$  in terms of the rate at which the object's entropy  $S$  increases with its internal energy  $U$ .  
**Limitations:** The derivative must be evaluated while holding all of the object's other macroscopic variables fixed (this is what the partial derivative symbol  $\partial S/\partial U$  means).

(You may have encountered partial derivatives already in unit E. If you have not, do not be stressed out by this new notation. A partial derivative is really the same thing as an ordinary derivative, except that the funny notation reminds us to hold everything that  $S$  might depend on except for  $U$  constant when we evaluate the derivative with respect to  $U$ .)  
 Since in principle we can count the number of microstates available to an object in a given macropartition, and from that determine how  $S \equiv k_B \ln \Omega$  varies with internal energy, we can calculate any object's temperature  $T$  from very fundamental physical quantities. *This is an extremely important equation!* The rest of this unit will be almost exclusively focused on exploring its implications.

### Exercise T6X.3

Show that having Boltzmann's constant  $k_B$  in the definition  $S \equiv k_B \ln \Omega$  ensures that the temperature  $T$  defined by equation T6.6 has units of kelvins.

## T6.2 Consistency with the Old Definition

Equation T6.6 defines temperature  $T$  in a manner consistent with the convention that heat flows from objects with large values of  $T$  to objects with low values of  $T$ . However, this in itself does not ensure that the temperature scale so defined is consistent with the old gas thermometer scale. In this section, we will see evidence suggesting that these two scales are in fact equivalent. We saw in chapter T2 that at sufficiently high temperatures, the thermal energy  $U$  of a monatomic solid satisfies the relationship

$$U = 3Nk_B T \quad \Rightarrow \quad \frac{1}{3Nk_B} = \frac{T}{U} \quad (\text{T6.7})$$

where  $T$  in this equation was the old gas thermometer temperature. But we know the multiplicity of an Einstein solid, so in principle we can use equation T6.6 to *calculate*  $1/T$  for a monatomic solid (modeled as an Einstein solid) as predicted by the new definition. If we get the same result, it will be strong evidence that our new definition of temperature coincides with the old.