

# Macrostates and Microstates

## Chapter Overview

### Section T2.1: The Einstein Model of a Solid

In this chapter, we will explore the roots of irreversibility with the help of a simple model of a solid. We can model a *monatomic* solid by imagining that each of its atoms oscillates independently around its equilibrium position in the solid lattice. 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 quantized 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  $h$  divided by  $2\pi$ . 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

The thermal energy of an Einstein solid

$$U = \sum_{i=1}^{3N} \epsilon n_i \quad \text{where} \quad \epsilon = \hbar \sqrt{\frac{k_s}{m}} \quad (\text{T2.5})$$

- **Purpose:** This equation specifies the total thermal energy  $U$  of an Einstein solid whose  $N$  atoms we model as  $3N$  identical but independent quantum oscillators, where  $n_1, n_2, n_3, \dots$  are a set of nonnegative integers (three per atom),  $\epsilon$  is the fixed difference between each oscillator's energy levels,  $\hbar \equiv h/2\pi$ ,  $h$  is Planck's constant,  $k_s$  is the effective spring constant of the interactions holding an atom in place, and  $m$  is the mass of one of the solid's atoms.
- **Limitations:** The Einstein model works well for monatomic solids at temperatures above 100 K or so (the exact limit depends on the solid).

### Section T2.2: Distinguishing Macrostates and Microstates

The core of Boltzmann's solution to the problem of irreversibility is the distinction between *macrostates* and *microstates*. We describe a system's **macrostate** by listing its variable macroscopic properties: for an Einstein solid, stating the solid's thermal energy  $U$  and its number of atoms  $N$  is sufficient to specify its macrostate. We describe a system's **microstate** by specifying the quantum state of every molecule in the system: for an Einstein solid, this amounts to specifying  $n_i$  for  $i = 1$  to  $3N$ . In principle, we can calculate a system's macroscopic properties (and thus its macrostate) if we know its microstate. In general, there are an immense number of microstates corresponding to any given macrostate; for example, we can distribute energy in many different ways among an Einstein solid's atoms without affecting its macroscopic total energy  $U$ .



## Section T2.3: Counting Microstates

The advantage of starting with the Einstein solid is that we can count the microstates in a given macrostate relatively easily (at least compared to many other physical systems). The **multiplicity**  $\Omega$  of a macrostate with energy  $U$  and number of atoms  $N$  is simply the number of different ways we can add  $3N$  integer multiples of  $\epsilon$  to get  $U$ . The general formula (see problem T2D.3) turns out to be

$$\Omega(U, N) = \frac{(q + 3N - 1)!}{q!(3N - 1)!} \quad (\text{T2.7})$$

- **Purpose:** This equation specifies the multiplicity  $\Omega$  of any macrostate of an Einstein solid, where  $N$  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, and  $n!$  or **n factorial**  $\equiv 1 \cdot 2 \cdot 3 \cdots (n - 1) \cdot n$ .
- **Limitations:** This equation applies *only* to an Einstein solid.

## Section T2.4: 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 (a certain macroscopic partitioning of the system's fixed total energy) by specifying the macrostate of each solid. A **macropartition table** lists all the combined system's macropartitions and their multiplicities. Table T2.1 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 T2.5: The Fundamental Assumption

The **fundamental assumption** of statistical mechanics is that *all of 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  $U_A = U_B = 3\epsilon$  macropartition in table T2.1 about  $100/28 = 3.6$  times more often than either the  $U_A = 0$  or  $U_B = 0$  macropartitions.

## Section T2.6: 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 web application StatMech (at <http://www.physics.pomona.edu/sixideas/resources.html>) constructs such tables for larger systems.

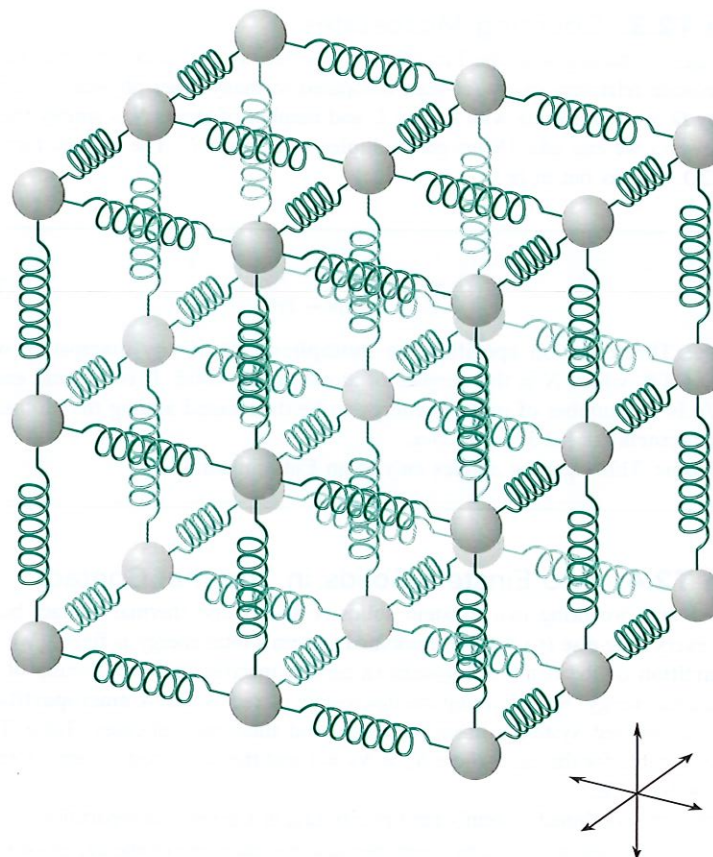
## Section T2.7: The Emergence of Irreversibility

When we use StatMech to create tables for larger Einstein-solid systems (involving thousands of atoms), we see that (1) the number of microstates becomes *extremely* (almost incomprehensibly) huge, but (2) the vast majority are in an increasingly narrow range around the most probable macropartition. This implies that purely random energy transfers in a sufficiently large system (1) will cause its macropartition to march inexorably toward the most probable (equilibrium) macropartition, and (2) upon arrival the system will subsequently visit in macropartitions within only an infinitesimal region near the most probable macropartition. The number of microstates in macropartitions far from the equilibrium macropartitions are so *incredibly* much smaller that moving *away* from equilibrium is impossible in any practical sense. This is why a heat transfer is irreversible.

**Table T2.1** Table of possible macropartitions for  $N_A = N_B = 1$ ,  $U = 6\epsilon$

$U_A/\epsilon$	$U_B/\epsilon$	$\Omega_A$	$\Omega_B$	$\Omega_{AB}$
0	6	1	28	28
1	5	3	21	63
2	4	6	15	90
3	3	10	10	100
4	2	15	6	90
5	1	21	3	63
6	0	28	1	28
Total microstates =				462



**Figure T2.1**

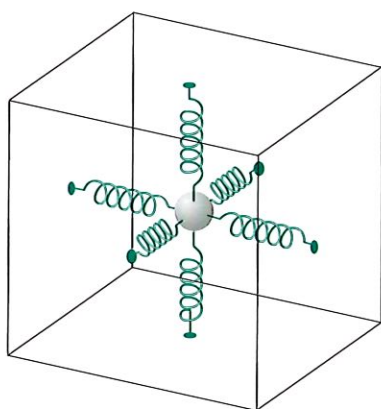
We can model the interactions between atoms in a crystalline monatomic substance as springs.

### T2.1 The Einstein Model of a Solid

In this chapter, we begin exploring Boltzmann's solution to the puzzle of irreversibility. We will be able to understand this solution most easily with the help of a very simple model of 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 crystalline solids (such as crystals of pure carbon, iron, or gold). Atoms in such a solid are held in nearly fixed positions in the crystal lattice by complicated interatomic electromagnetic interactions. However, as long as the atoms remain close to their equilibrium positions (where their interaction potential energy functions are minimum), we saw in chapter C9 that we can approximate the potential energy function for almost any interaction by that for a spring, so we can (as a first approximation) model all the interatomic interactions as if they were springs (see figure T2.1).

Even in such a model, the atoms can affect each other in complicated ways, so Einstein proposed a further simplification: assume that each atom oscillates *independently* about its equilibrium position, behaving as if it were connected by springs to the rigid walls of its individual "cell" in the crystal lattice instead of being interconnected with the surrounding atoms (see figure T2.2). So in this model, we assume that each atom's potential energy when it is a distance  $r$  from its equilibrium position is  $\frac{1}{2}k_s r^2$  (where  $k_s$  is the effective spring constant of the interactions that hold the atom in place) independent of both the direction of  $r$  and the positions of neighboring atoms. The model also assumes that each atom is identical, meaning that the spring constant  $k_s$  is the same for all atoms. Einstein

**Figure T2.2**

In Einstein's model, we treat each atom as independent, as if its springs were connected to the rigid walls of its "cell."

was able to show (as we will see) that this simplistic model nonetheless accurately describes the thermal behavior of monatomic solids over a wide temperature range.

Now, 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 oscillator is

$$\begin{aligned} E &= \frac{1}{2}m|\vec{v}|^2 + \frac{1}{2}k_s r^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) + \frac{1}{2}k_s(x^2 + y^2 + z^2) \\ &= (\frac{1}{2}mv_x^2 + \frac{1}{2}k_s x^2) + (\frac{1}{2}mv_y^2 + \frac{1}{2}k_s y^2) + (\frac{1}{2}mv_z^2 + \frac{1}{2}k_s z^2) \end{aligned} \quad (\text{T2.1})$$

where  $m$  is the atom's mass. Note how we can group the terms in the energy equation 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 T2D.5) that the 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 spring potential energy function: most other potential energy functions cannot be pulled apart in this way.)

According to quantum mechanics (see chapter Q10), the energy associated with each of these separate one-dimensional oscillations is *quantized*, so that the atom's total vibrational energy is given by

$$E = \hbar\omega(n_x + \frac{1}{2}) + \hbar\omega(n_y + \frac{1}{2}) + \hbar\omega(n_z + \frac{1}{2}) \quad (\text{T2.2})$$

where  $\omega = (k_s/m)^{1/2}$  is the angular frequency of the equivalent Newtonian oscillator and  $\hbar \equiv h/2\pi$ , 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. See unit Q for a justification of this: for our purposes at the present it is enough simply to know that this is true.

We can rewrite this equation as

$$E = \sum_{i=1}^3 \hbar\omega(n_i + \frac{1}{2}) = \sum_{i=1}^3 \varepsilon(n_i + \frac{1}{2}) \quad (\text{T2.3})$$

where  $\varepsilon \equiv \hbar\omega = \hbar(k_s/m)^{1/2}$  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):

$$E_{\text{tot}} = \sum_{i=1}^{3N} \varepsilon \left( n_i + \frac{1}{2} \right) = \sum_{i=1}^{3N} \varepsilon n_i + \sum_{i=1}^{3N} \frac{1}{2} \varepsilon = \sum_{i=1}^{3N} \varepsilon n_i + \frac{3}{2} N \varepsilon \quad (\text{T2.4})$$

The constant  $\frac{3}{2}N\varepsilon$  term in this equation is called the solid's **zero-point energy**. The solid will have this energy even at absolute zero (which is the temperature where all atoms are in their *lowest possible* energy state, by definition) and it cannot be affected by the solid's interaction with its surroundings: it is a built-in aspect of the solid's internal energy. We define a system's *thermal* energy  $U$  to be that part of the system's internal energy that *changes* when the system's temperature changes due to its interactions with other objects (assuming that the system's phase, chemical composition, and nuclear composition remain fixed). So, this zero-point energy (along with the internal energies of all the atoms) is not part of the solid's *thermal* energy  $U$ . We can therefore write the solid's thermal energy as

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

The quantum zero-point energy of the solid is irrelevant



The thermal energy of an Einstein solid

$$U = \sum_{i=1}^{3N} \epsilon n_i \quad \text{where} \quad \epsilon = \hbar \sqrt{\frac{k_s}{m}} \quad (\text{T2.5})$$

- **Purpose:** This equation specifies the total thermal energy  $U$  of an Einstein solid whose  $N$  atoms we model as  $3N$  identical but independent quantum oscillators, where  $n_1, n_2, n_3, \dots$  are a set of nonnegative integers (three per atom),  $\epsilon$  is the fixed difference between each oscillator's energy levels,  $\hbar \equiv h/2\pi$ ,  $h$  is Planck's constant,  $k_s$  is the effective spring constant of the interactions holding an atom in place, and  $m$  is the mass of one of the solid's atoms.
- **Limitations:** The Einstein model works well for monatomic solids at temperatures above 100 K or so (the exact limit depends on the solid).

Note that because  $\epsilon \propto (k_s/m)^{1/2}$ , it increases as the strength of the interatomic forces increases, and decreases as the mass of each of the atoms increases.

The basic point of equation T2.5 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  $\epsilon$ .* We will call any solid accurately described by this model an **Einstein solid**.

## T2.2 Distinguishing Macrostates and Microstates

The core step in understanding Boltzmann's solution to the problem of irreversibility is to understand the crucial distinction between the *macrostate* and the *microstate* of a thermodynamic system.

Definition of *macrostate*

A system's **macrostate** is that system's thermodynamic state as characterized by its *macroscopically measurable and potentially variable properties*. These are properties of the system *as a whole* that might in principle change as the system interacts thermally with its surroundings. These properties include the system's total thermal energy  $U$ , its temperature  $T$ , its volume  $V$ , the number of particles  $N$  that it contains, its mass  $M$ , and so on.

We can completely describe a system's macrostate by specifying some *minimal* set of macroscopic properties that suffice to calculate all its *other* macroscopic properties. For example, a monatomic solid's thermal energy  $U$  is connected to its temperature  $T$  and the number of particles  $N$  (see equation T1.5), so if we specify  $U$  and  $N$ , we can in principle calculate  $T$ . The solid's mass  $M = mN$ , where  $m$  is the mass of an atom. As the atom's mass does not depend on the system's external circumstances, it does not count as a *variable* property, so knowing  $N$  determines  $M$ . Under normal circumstances, a solid's density is also pretty much fixed, so knowing  $N$  also determines the solid's volume  $V$ . We see, therefore, that knowing  $U$  and  $N$  pretty much fixes a solid's macrostate under normal circumstances. On the other hand, the density of a gas (or a solid under extreme pressure) might vary dramatically, so we might have to add another macroscopic variable (for example, the system's volume  $V$ ) to completely describe such a system's macrostate.

Definition of *microstate*

A system's **microstate**, on the other hand, is characterized by describing the quantum state of *each individual molecule* in the system at a given time. In the case of an Einstein solid, this means specifying the quantum state of (that is, the value of  $n$  for) each of the system's  $3N$  independent oscillators. Note that while this idea is conceptually straightforward, even the tiniest speck of solid contains so many atoms that describing the speck's microstate would be impossible in practice, but we can at least *imagine* doing it.



Note that if we know a system's microstate, we know its macroscopic properties as well. If we know the value of  $n$  for every oscillator in an Einstein solid, then we implicitly know  $N$  and can calculate  $U$  using equation T2.5, so we know what we need to specify the solid's macrostate.

Now, the most important thing to understand about microstates and macrostates is that a system in a given, well-specified macrostate could be in any one of a *huge* number of different microstates that we are unable to distinguish by macroscopic measurements. For example, suppose that we describe an Einstein solid's macrostate by stating values for  $U$  and  $N$ . There are many possible microstates that nonetheless add up to the same total  $U$  (each simply corresponds to a different way of distributing that total energy among  $3N$  oscillators). 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 bedroom. 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, a fairly large number of arrangements of objects in your room might qualify the room as being "clean" (for example, there are a number of possible ways to neatly 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.

There are *many* microstates in a macrostate

## T2.3 Counting Microstates

Why begin our journey with the Einstein solid? The answer is that we can *much* more easily calculate the number of microstates corresponding to each macrostate of an Einstein solid than for any other reasonably realistic thermodynamic model. This in turn makes it comparatively easier to determine what statistical physics predicts about this model. Models of other complex systems behave in *qualitatively* similar ways, so what we learn from this model applies at least qualitatively to other systems as well. We will also use this model to develop tools that help us handle more complex models.

As we saw in the last section, we can describe an Einstein solid's macrostate by specifying its thermal energy  $U$  and its number of atoms  $N$ . To describe the solid's microstate, we must specify an integer value  $n_i$  for each of the solid's  $3N$  independent oscillators. In general, there will be *many* microstates (that is, many distinct sets of values for all  $3N$  integers  $n_i$ ) that have the same total  $U$ . We call the number of possible microstates that correspond to the same given macrostate that macrostate's **multiplicity**  $\Omega$ . In the case of an Einstein solid, where the macrostate is specified by  $U$  and  $N$ ,

$$\begin{aligned}\Omega(U, N) &\equiv \text{the multiplicity of the macrostate specified by } U \text{ and } N \\ &= \text{the number of } N\text{-atom microstates having total energy } U\end{aligned}\quad (\text{T2.6})$$

How can we determine  $\Omega(U, N)$  for given values of  $U$  and  $N$ ? The beauty of the Einstein solid model is that this is not a *conceptually* difficult problem. According to equation T2.5, the total energy in an Einstein solid is an integer multiple of the basic energy unit  $\epsilon$ . Think of each energy unit as a marble, and each of the solid's  $3N$  oscillators as a bin into which we can put marbles. When we specify the solid's total energy  $U$ , we are essentially specifying the total number of "marbles"  $q \equiv U/\epsilon$  that we must distribute. Counting the microstates for this  $U$ , then,

Describing the macrostate of an Einstein solid

Counting microstates



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

is the same as counting how many different ways we can sort  $q$  marbles into  $3N$  bins.

In a solid of macroscopic size,  $3N$  will be on the order of magnitude of  $10^{23}$ , but let's start small. Suppose our Einstein solid consists 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 (that is, 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, and so on.

So let us start counting microstates for various different macrostates of this one-atom Einstein solid. First, suppose the solid's total energy has its lowest possible value  $U = 0$ . Only one microstate (000) is compatible with this total energy, so this macrostate's multiplicity is  $\Omega(U, N) = \Omega(0, 1) = 1$ .

Now suppose the solid's total energy 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. This macrostate's multiplicity is thus  $\Omega(1\varepsilon, 1) = 3$ . If the solid's total energy is  $U = 2\varepsilon$ , then the possible microstates are 002, 020, 200, 110, 101, 011, so this macrostate's multiplicity is  $\Omega(2\varepsilon, 1) = 6$ . In a similar fashion, one can show that  $\Omega(3\varepsilon, 1) = 10$ ,  $\Omega(4\varepsilon, 1) = 15$ ,  $\Omega(5\varepsilon, 1) = 21$ , and  $\Omega(6\varepsilon, 1) = 28$ .

### Exercise T2X.1

Verify that  $\Omega(3\varepsilon, 1) = 10$  by writing down all possible microstate triplets consistent with this macrostate and counting them.

An Einstein solid with two atoms (six independent oscillators) and zero total energy has one microstate 000000, so  $\Omega(0, 2) = 1$ . If the solid's total energy is  $U = \varepsilon$ , then the possible microstates are 000001, 000010, 000100, 001000, 010000, and 100000, so  $\Omega(1\varepsilon, 2) = 6$ . When  $U = 2\varepsilon$ , the possible microstates are 000002, 000020, 000200, 002000, 020000, and 200000, 000011, 000101, 001001, 010001, 100001, 000110, 001010, 001100, 010010, 010100, 011000, 100010, 100100, 101000, and 110000, so  $\Omega(2\varepsilon, 2) = 21$ . In a similar fashion, one can show that  $\Omega(3\varepsilon, 2) = 56$ ,  $\Omega(4\varepsilon, 2) = 126$ , and so on.

Counting microstates this way gets pretty tedious after a while. However, one can prove generally that if  $q = U/\varepsilon$  is the total number of energy units to be distributed among  $3N$  oscillators, then

The multiplicity of an Einstein solid's macrostate

$$\Omega(U, N) = \frac{(q + 3N - 1)!}{q!(3N - 1)!} \quad (\text{T2.7})$$

- **Purpose:** This equation specifies the multiplicity  $\Omega$  of any macrostate of an Einstein solid, where  $N$  is the number of atoms in the solid,  $U$  is its total energy,  $q \equiv U/\varepsilon$  is the number of units of energy to be distributed among the atoms, and  $n!$  or **n factorial**  $\equiv 1 \cdot 2 \cdot 3 \cdots (n - 1) \cdot n$ .
- **Limitations:** This equation applies *only* to an Einstein solid.

(Problem T2D.3 shows how to derive this formula.) So, for example,

$$\begin{aligned}\Omega(4\epsilon, 2) &= \frac{(4+6-1)!}{4!(6-1)!} = \frac{9!}{4!5!} = \frac{9 \cdot 8 \cdot 7 \cdot 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1}{(4 \cdot 3 \cdot 2 \cdot 1)(5 \cdot 4 \cdot 3 \cdot 2 \cdot 1)} \\ &= \frac{9 \cdot 8 \cdot 7 \cdot 6}{4 \cdot 3 \cdot 2 \cdot 1} = 9 \cdot 7 \cdot 2 = 126\end{aligned}\quad (\text{T2.8})$$

### Exercise T2X.2

(a) Check that equation T2.7 yields the same results for  $\Omega(0, 1)$ ,  $\Omega(\epsilon, 1)$ ,  $\Omega(2\epsilon, 1)$ , and  $\Omega(2\epsilon, 2)$  that we found earlier by direct counting. (b) Use equation T2.7 to verify that  $\Omega(6\epsilon, 1) = 28$ . (c) If an Einstein solid has *three* atoms, what is the multiplicity of the macrostate where it has 8 units of energy?

## T2.4 Two Einstein Solids in Thermal Contact

Suppose now we bring two Einstein solids *A* and *B*, one with  $N_A$  atoms ( $3N_A$  oscillators) and one with  $N_B$  atoms ( $3N_B$  oscillators), into thermal contact, so that microscopic interactions between atoms on the surfaces in contact can allow energy to flow between the solids. How will these solids behave *macroscopically* after being brought into contact?

The values of  $N_A$  and  $U_A$  specify solid *A*'s macrostate, and  $N_B$  and  $U_B$  specify solid *B*'s macrostate. If we suppose that  $N_A$  and  $N_B$  are fixed, then just  $U_A$  and  $U_B$  sufficiently specify the solids' macrostates. 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's 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*.

Now, suppose that in a certain macropartition, solid *A* has energy  $U_A$  and multiplicity  $\Omega_A$ , and solid *B* has energy  $U_B$  and multiplicity  $\Omega_B$ . What is the macropartition's multiplicity? Well, for *each* of the  $\Omega_A$  microstates that solid *A* might be in, solid *B* could be in *any* of its  $\Omega_B$  microstates, so the total number of microstates consistent with this particular partitioning of the energy between solids *A* and *B* must be the *product* of these multiplicities:

$$\Omega_{AB} = \Omega_A \Omega_B \quad (\text{T2.9})$$

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

A macropartition's multiplicity



A macropartition table for Einstein solids in contact

**Table T2.1** Table of possible macropartitions for  $N_A = N_B = 1$ ,  $U = 6\epsilon$

$U_A/\epsilon$	$U_B/\epsilon$	$\Omega_A$	$\Omega_B$	$\Omega_{AB}$
0	6	1	28	28
1	5	3	21	63
2	4	6	15	90
3	3	10	10	100
4	2	15	6	90
5	1	21	3	63
6	0	28	1	28
Total microstates =				462

A specific example may make this clearer. Suppose that we bring two one-atom Einstein solids into thermal contact, and suppose that their total combined energy is  $U = 6\epsilon$ . Let's construct a table that lists in successive lines all the possible macropartitions for the combined system. On each line, we specify the macropartition by stating the two solids' energies  $U_A$  and  $U_B$  in units of  $\epsilon$ , the multiplicities  $\Omega_A$  and  $\Omega_B$  of their respective macrostates, and the macropartition's multiplicity  $\Omega_{AB} = \Omega_A\Omega_B$ . Table T2.1 shows such a **macropartition table**.

To see why  $\Omega_{AB} = \Omega_A\Omega_B$ , consider, for example, the macropartition where  $U_A = U_B = 3\epsilon$ . 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 T2X.3

Prepare an analogous table for the case where  $N_A = N_B = 1$  and  $U = 8\epsilon$ . (Use equation T2.7 to calculate the multiplicities you can't get from table T2.1.)

## T2.5 The Fundamental Assumption

In a real solid, the atoms can (and do) exchange energy through random microscopic processes. So to get the Einstein model to fit reality, we must assume that adjacent atoms *do* interact enough to exchange energy, but not *so* strongly that the energy-level structure of each quantum oscillator is significantly affected. Energy will also shift randomly back and forth across the boundary between the solids due to interactions between atoms on the surfaces in contact.

Therefore, as time passes, a combined system of two Einstein solids will randomly shift between different microstates consistent with the constraint that the total energy has 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 T2.1, the combined system in microstate 012-300 (one of the microstates corresponding to the macropartition where  $U_A = U_B = 3\epsilon$ ) might evolve to 013-200 (one of the microstates corresponding to macropartition  $U_A = 4\epsilon$ ,  $U_B = 2\epsilon$ ) by transferring 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.

Now comes the big question: Can we say something about which macropartitions we are most *likely* to see if we peek at the system at various times? We can indeed, if we are willing to accept a simple and plausible assumption:

An isolated system's accessible microstates are all *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.") We call this statement the **fundamental assumption** of statistical mechanics.

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

The fundamental assumption of statistical mechanics