

Chapter 9

Second Law of Thermodynamics and Entropy

In this chapter we will discuss one of the most significant developments in the history of science — the development of a *statistical* theory of thermodynamics. Here is the question: if a chunk of ice, or a glass of water, or an air-filled balloon is composed of 10^{22} or 10^{23} molecules, isn't it necessary to describe the dynamics of each individual molecule? To determine the force on each molecule and solve Newton's second law to figure out its motion? The answer is no, thankfully. Instead, we can treat each of these molecules as though they are behaving randomly, and recover all the results of thermodynamics from a probabilistic treatment.

The importance of this statistical approach cannot be overstated. The idea that we can treat thermodynamic systems probabilistically led to a revolution in scientific thought that ranks up there with Newton's development of classical physics, Pasteur's development of germ theory of disease, Einstein's theory of relativity, and the development of quantum mechanics (which you'll see in PHYS 212).

We will introduce statistical mechanics by revisiting the basic phenomenon of heat flow, the spontaneous thermal energy transfer from hotter objects to colder objects. The direction of the heat flow is determined by what is known as the *second law of thermodynamics*. We can derive the second law of thermodynamics from probability arguments; essentially, thermal energy flow is dictated by moving from an improbable to a probable situation. Entropy is introduced as a measure of probability. And along the way to understanding the second law, we will provide a general definition of temperature.

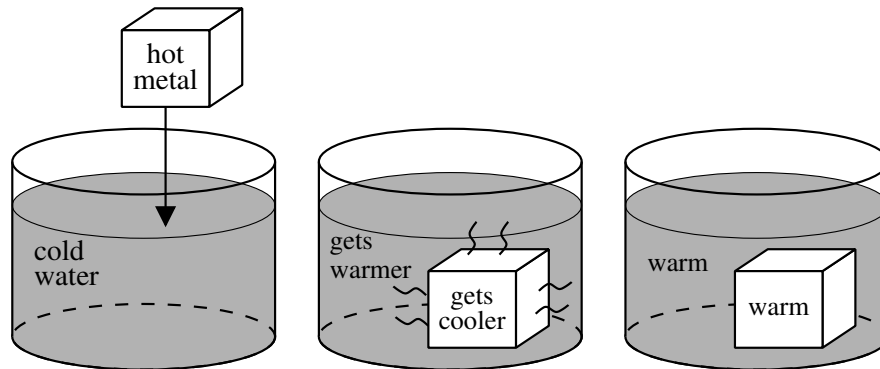


Figure 9.1: A hot piece of metal is placed into cold water. Thermal energy is transferred from the hot metal to the cold water until they are in thermal equilibrium.

9.1 Heat Flow Revisited

Consider the following process, illustrated in Fig. 9.1: a hot piece of metal is placed into a container holding cold water. As time passes, thermal energy flows from the metal to the water, making the metal colder and the water warmer. Eventually, the two are at the same temperature and no more thermal energy is transferred. This is *heat*: the spontaneous thermal energy transfer due to the temperature difference, as we identified in section 6.10.

In a heat flow scenario, such as this one, the first law of thermodynamics states that energy is conserved, and so we must have

$$\Delta E_{\text{therm,water}} = -\Delta E_{\text{therm,metal}}. \quad (9.1)$$

However, energy conservation would be equally well satisfied if the heat flowed the other way. Imagine putting the hot metal into cold water and finding that the metal becomes increasingly hotter while the water becomes increasingly cooler, beginning to freeze. Absurd! This is never observed to happen. And yet it would be perfectly consistent with the first law of thermodynamics.

What this process illustrates is that there must be an additional law of nature involved that determines the direction of heat flow. In a fit of creativity, physicists decided to call this the *second* law of thermodynamics. There are many equivalent ways to state the second law. We will begin with the *Clausius statement* of the second law, since it is the most intuitive.

2ND LAW OF THERMODYNAMICS (CLAUSIUS):
Heat cannot flow spontaneously from a material at lower temperature to a material at higher temperature.

Let's examine this. First, note that the law is, at this point, empirical, which means it is a statement about the observed behavior of nature. The second law rules out the absurd scenario whereby heat flowed from the cold water to the hot metal. But, note that the second law makes no statement about whether the heat will actually flow from the metal to the water. According to the second law, this heat flow is allowed, but not required. That is exactly what we want from a general law, since after all the metal and the water may or may not be thermally coupled.

Temperature plays a crucial role in the second law, since the question of whether heat is allowed to flow from A to B or instead from B to A is answered by the temperatures T_A and T_B . Temperature plays the role of nature's traffic cop, enforcing thermodynamic "one-way streets."¹ The primary topic of this chapter is the explanation of why temperature plays this role.

Another interesting aspect of the second law is the phenomenon of *irreversibility*. Many processes in nature are reversible. A movie of the flight of a ball thrown straight up into the air, turning around and coming back down, looks the same whether played forward or backward. This is because Newton's law are *reversible* as long as friction is negligible. But once heat flows from the hot metal to the cold water, it will never spontaneously flow back again. A movie of the process (with some thermometers used to make the temperature visible) would look different played backward versus forward. Physicists believe the second law is the origin of any irreversibility observed in nature, which is to say, the second law of thermodynamics plays a crucial role in determining the direction of time flow.

Interestingly, the second law is unique among laws of physics. Most laws are simply inferred from the behavior of nature. We don't know why energy conservation happens; we just know it does. The second law is different because we can essentially derive it. We know *why* it happens. It is ultimately a statement about probability: thermal energy flows spontaneously from hotter objects to colder objects because that brings the system to a state with a more likely arrangement of energy.

The rest of this chapter is concerned with expanding our probabilistic understanding of the second law and temperature.

9.2 Microstates, Macrostates, and Multiplicity

To explain how probabilities work in thermodynamics — and ultimately to explain entropy and how it relates to the second law of thermodynamics — it is necessary to discuss some fundamental concepts of probability. We start with definitions of *microstates* and *macrostates*:

¹However, nature needs no traffic court since its one-way streets, like its speed limit, are self-enforcing.

A *macrostate* is a specification of the macroscopic state of the system. For example, the pressure, temperature, and number of moles of an ideal gas would specify a macrostate.

A *microstate* is the detailed specification of the microscopic state of the system. In the ideal gas example, the microstate would be precise values for the position and velocity of every single molecule.

A macrostate can have many microstates associated with it. In the ideal gas example, there are many possible arrangements of the molecules that are consistent with having, say, one mole of gas with atmospheric pressure and room temperature. This brings us to multiplicity:

The *multiplicity* Ω of a macrostate is the number of microstates associated with that macrostate.

Let's explore these ideas with a specific example: a pair of six-sided dice, one red and one green.² There are 36 possible outcomes of rolling these dice, listed in Table 9.1, and the sum of the two dice can be any number between two and twelve. Not every sum is equally probable, however. If you roll the dice many times, you will notice you get a sum of seven much more often than, say, a sum of twelve.

The 36 possible outcomes are the microstates. The red dice showing '5' and the green die showing '3' would be a particular microstate (labeled 5-3 in Table 9.1). The sum of the dice, eight in this case, represents a macrostate. Notice that there are many ways to roll a sum of eight; or stated another way, there are multiple microstates associated with the macrostate '8.' The number of ways to roll an '8' is the multiplicity Ω . Looking at Table 9.1, we see there are five different ways to roll an '8', so the multiplicity $\Omega = 5$.

The multiplicity of a macrostate is useful to know because it tells us the probability of obtaining that particular macrostate. Each of the 36 microstates for a pair of dice is equally likely. The reason that a sum of seven is a more likely outcome than a sum of twelve is not because 4-3 is more likely than 6-6 (it's not!), rather, there are more ways to roll a '7.'

Now let's come back to physics. The macrostate of a collection of molecules could be defined in terms of the number of particles and the amount of energy E_{therm} they have. A microstate would correspond to a particular arrangement of the energy among the molecules. Since there are many possible ways to arrange the energy among the molecules, there are many microstates associated with this macrostate. The number of possible

²Having dice of the same color wouldn't change anything. We just use different colors to help label the dice.

sum	rolls (red die–green die)						Ω	probability
2	1-1						1	1/36
3	1-2	2-1					2	2/36 = 1/18
4	1-3	2-2	3-1				3	3/36 = 1/12
5	1-4	2-3	3-2	4-1			4	4/36 = 1/9
6	1-5	2-4	3-3	4-2	5-1		5	5/36
7	1-6	2-5	3-4	4-3	5-2	6-1	6	6/36 = 1/6
8	2-6	3-5	4-4	5-3	6-2		5	5/36
9	3-6	4-5	5-4	6-3			4	4/36 = 1/9
10	4-6	5-5	6-4				3	3/36 = 1/12
11	5-6	6-5					2	2/36 = 1/18
12	6-6						1	1/36

Table 9.1: The 36 possible results from rolling a pair of dice (one red, one green).

ways to arrange the given amount of energy would then be the multiplicity Ω .

To go from multiplicity to probability we need one more piece of information. In the case of the dice, each of the 36 possible outcomes was equally likely, assuming that the dice were fair, returning each of the six values with equal probability. Does this apply as well for our system of N particles sharing a total energy E_{therm} ? In general, we cannot prove this, but to make progress we will assume that it is true.

THE FUNDAMENTAL ASSUMPTION OF STATISTICAL MECHANICS:
All of a system's accessible microstates are equally likely.

“Accessible microstates” here means simply those which are allowed by energy conservation. The motivation for this assumption is that whatever the specific dynamics are, however the molecules are colliding and sloshing energy back and forth among each other, they eventually visit every possible state allowed by energy conservation. So a sequence of snapshots of the system would look like randomly selected examples of possible microstates. In the end, nature has confirmed that starting with the fundamental assumption leads to predictions that match experiments extremely well. Now we shall see what the fundamental assumption buys us.

9.3 Einstein Solid

We now develop the ideas of the previous section in the context of a specific model. The simplest model to work with, it turns out, is not the ball-

spring model or the ideal gas, but rather a variation of the ball-spring solid called the Einstein solid. Experiments on very cold metals showed that their specific heats could fall well below the value $3R$, suggesting something not contained in the ball-spring model was occurring at low temperatures. Einstein showed that a quantum mechanical version of the ball-spring model could explain this result.³ To begin, notice that a three-dimensional oscillator, such as the molecule in the ball-spring model, can be written as a sum of three independent, one-dimensional oscillators:

$$\begin{aligned} E_{\text{ball}} &= \left(\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2\right) + \left(\frac{1}{2}k_{sp}x^2 + \frac{1}{2}k_{sp}y^2 + \frac{1}{2}k_{sp}z^2\right) \\ &= \left(\frac{1}{2}mv_x^2 + \frac{1}{2}k_{sp}x^2\right) + \left(\frac{1}{2}mv_y^2 + \frac{1}{2}k_{sp}y^2\right) + \left(\frac{1}{2}mv_z^2 + \frac{1}{2}k_{sp}z^2\right) \quad (9.2) \end{aligned}$$

In the second grouping, each term in parentheses is an oscillator moving in one particular direction and independent of the motion in the other perpendicular directions. Thus a set of N molecules in the ball-spring model is equivalent to $3N$ one-dimensional oscillators. In what follows we will be working primarily with the one-dimensional oscillators so we let N represent the number of oscillators instead of the number of molecules. The number of molecules is then $N/3$.

Einstein proposed to treat the one-dimensional oscillators quantum mechanically, which should be appropriate when the temperature is low enough. We will not discuss quantum mechanics here — that is a topic for PHYS 212 — but we will summarize the main results of interest to us. The energy levels of the quantum harmonic oscillator are not continuous but rather discrete (or *quantized*). This is illustrated in Fig. 9.2. At very low energies we cannot vary the oscillator energy up or down by arbitrarily small amounts, but rather can only add energy in discrete chunks. Furthermore, for the quantum harmonic oscillator, these energy levels are equally spaced. Therefore we can write the energy level of an oscillator as

$$E_{\text{osc}} = E_0 + n\epsilon \quad \text{where } n = 0, 1, 2, 3, \dots \quad (9.3)$$

Here E_0 is the lowest energy level possible, and we may increase the energy by adding an integer number of “energy units” of size ϵ .

Now consider a system of two oscillators, with a total energy of three “energy units.” These oscillators bounce energy back and forth and so one of the oscillators may have at a given instant anywhere from zero to all three of the energy units. Let n_1 be the number of energy units that the first oscillator has, and n_2 the number of energy units for the second oscillator. Specifying n_1 and n_2 determines a particular microstate. The total energy

³The complete description of very cold metals requires an additional modification, worked out by a Dutch physicist named Peter Debye. We will not consider the Debye theory here.

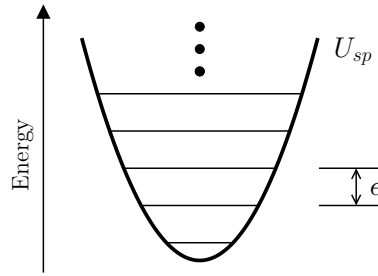


Figure 9.2: The quantum harmonic oscillator has discrete energy levels, shown as horizontal lines. The energy difference between successive levels is ϵ .

of three units implies $n_1 + n_2 = 3$, so the possible microstates, written as (n_1, n_2) , are

$$(3, 0), \quad (2, 1), \quad (1, 2), \quad (0, 3).$$

Evidently, the multiplicity of the macrostate with two oscillators and a total of three energy units is $\Omega = 4$. That is, there are four different microstates with this total energy.

Example 9.1 Three oscillators, two energy units

Write down all the microstates for a system of three oscillators and a total of two energy units, and determine the multiplicity.

Solution: For microstates written as (n_1, n_2, n_3) , we need to have $n_1 + n_2 + n_3 = 2$, so the possible microstates are

$$(2, 0, 0), \quad (0, 2, 0), \quad (0, 0, 2), \quad (1, 1, 0), \quad (1, 0, 1), \quad (0, 1, 1),$$

and the multiplicity $\Omega = 6$.

It is feasible to determine the multiplicity directly by counting the microstates when the number of oscillators and energy units is small. But this becomes unwieldy very quickly as the number of oscillators and energy units is increased. Fortunately, we can derive the general result for N oscillators and q total energy units, which is

$$\Omega = \frac{(q + N - 1)!}{q! (N - 1)!}. \quad (9.4)$$

The factorial function is defined as $n! = n(n-1)(n-2) \cdots 2 \cdot 1$. For example, $5! = 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1 = 120$. A special case is the factorial of the number zero:

by definition, $0! = 1$. The meaning of $n!$ is that it is the number of distinct ways to order n objects. The number of ways to order zero objects is taken to be 1.

Example 9.2 Checking the multiplicity formula.

Verify the Einstein solid multiplicity formula, Eq. (9.4), for the cases of two oscillators with three energy units and three oscillators with two energy units.

Solution: For two oscillators and three energy units ($N = 2$ and $q = 3$) the multiplicity formula gives

$$\Omega = \frac{(3 + 2 - 1)!}{3! (2 - 1)!} = \frac{4!}{3! 1!} = \frac{24}{6 \cdot 1} = 4, \quad (9.5)$$

which matches our result above. For the second case, $N = 3$ and $q = 2$, giving

$$\Omega = \frac{(2 + 3 - 1)!}{2! (3 - 1)!} = \frac{4!}{2! 2!} = \frac{24}{2^2} = 6, \quad (9.6)$$

verifying the second case.

Factorials become very large very quickly. For example, $100! \approx 10^{157}$, which is an amazingly large number. An Einstein solid with 100 oscillators and 200 energy units has a multiplicity $\Omega = 2.8 \times 10^{82}$. Now you can appreciate having Eq. (9.4) to work with instead of counting all possible microstates. And imagine how large the result would be for Avogadro's number of oscillators!

9.4 Coupled Einstein Solids

Our original goal was to understand heat flow. That is, why thermal energy spontaneously goes from hotter objects to colder objects. To that end, we will now consider two Einstein solids, solid A with a number N_A oscillators and q_A energy units, and solid B with N_B oscillators and q_B energy units. If solids A and B are brought into thermal contact, then they will be able to pass energy units back and forth while maintaining a fixed total $q_{\text{tot}} = q_A + q_B$. But which way will the energy go, on average? And when will it come to thermal equilibrium? Let us try to address these questions.

q_A	q_B	Ω_A	Ω_B	Ω_{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

Table 9.2: Possible macrostates for system A and B sharing six units of energy, with $N_A = 3$ and $N_B = 3$.

Once the two Einstein solids are thermally coupled and exchanging energy, A and B should be regarded as *subsystems* of the combined system. For a particular division of energy among the two subsystems, we have a multiplicity Ω_A that depends on N_A and q_A , and a multiplicity Ω_B that depends on N_B and q_B .

How do we calculate the combined multiplicity of the system? If you have three pairs of pants and five shirts, then you have $3 \cdot 5 = 15$ possible combinations you can make, at least in polite company. Similarly, subsystem A may be in any of the number Ω_A microstates and subsystem B in any of Ω_B microstates, so the number of paired microstates we can make is the product $\Omega_{AB} = \Omega_A \Omega_B$. This is the combined multiplicity of the system.

Let's consider a specific case. Let $N_A = 3$ and $N_B = 3$, and $q_{\text{tot}} = q_A + q_B = 6$. The two systems may divide up the six energy units a variety of ways, as shown in Table 9.2. For each choice, the multiplicities Ω_A and Ω_B and the combined multiplicity Ω_{AB} are given. Note that the most probable arrangement of energy, the one with the largest multiplicity, is the one with three energy units in each subsystem. If subsystem A started with zero energy units and subsystem B with six units, then simple random energy exchanges would move the coupled systems toward the more probable state with $q_A = q_B = 3$. This is a clue about the origin of the second law.

From Table 9.2 we see that the most probable situation is only slightly more probable than the other possibilities. This changes dramatically as the system size is increased. In Fig. 9.3 we plot the combined multiplicity as a function of q_A for various numbers of oscillators and energy units. As the figure shows, when the numbers become larger, say in the thousands, the multiplicity function becomes sharply peaked. Some particular division of energy between the two subsystems is vastly, hugely, awesomely, mind-bogglingly more probable⁴ than all others. This we identify as the equilibrium division of energy. Now imagine what occurs when you approach Avogadro's number

⁴I.e., it isn't just a little more probable, it is a **lot** more probable.

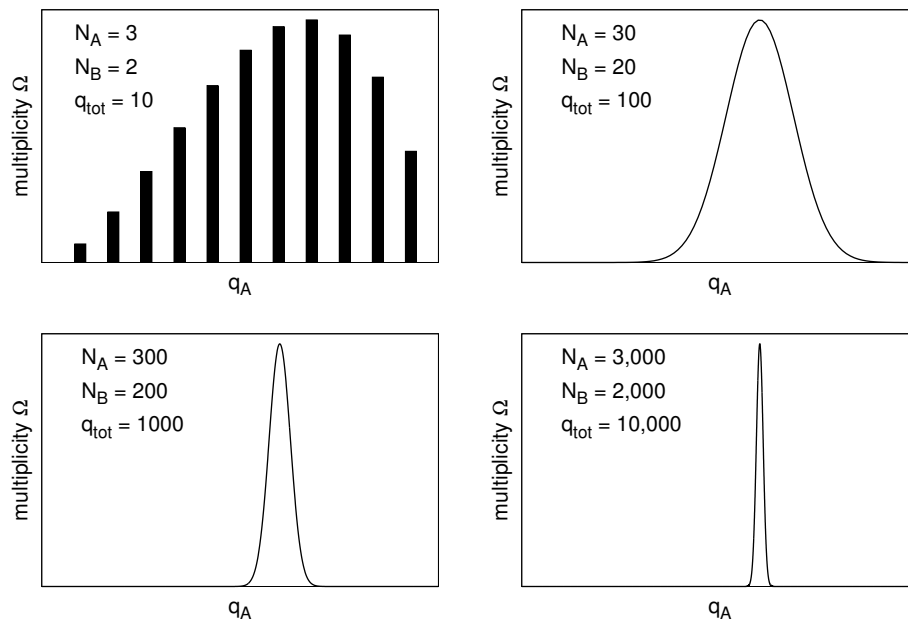


Figure 9.3: Plots of the multiplicity as a function of q_A for a variety of system sizes. Note that q_B is determined by $q_A + q_B = q_{\text{tot}}$.

of energy units. The multiplicity function becomes completely sharp. There is some particular division of the energy between subsystems A and B that is ridiculously, overwhelmingly, staggeringly⁵ more probable than any other.

Now we have the probabilistic origin of the second law. Subsystems A and B , before they are thermally coupled, can be prepared with any thermal energy we would like. We made the metal object hot and the water cold before plunging the metal into the water. But once the subsystems are thermally coupled, they will move from whatever division of energy they started with toward the maximally probable arrangement of energy for the coupled system. They are irresistibly led to it by essentially random exchanges of energy between the subsystems. The energy transferred along the way is what we had previously identified as heat.

To summarize:

The second law of thermodynamics is a result of a system prepared in an improbable initial state then moving to a vastly more probable final state.

⁵“...vastly, hugely, awesomely, mind-bogglingly, ...” and that doesn’t even begin to cover it!

This is an incredibly important result!!!! With this statement, we don't have to worry at all about the detailed, Newtonian mechanics of the (many, many) individual molecules or atoms in a solid, liquid or gas. We treat all the motion as though it is random and then simply figure out the probabilities.

9.5 Entropy

Entropy is part of the title of the chapter; perhaps it is time we introduced it. The fact is, we have already been discussing the entropy, because entropy is simply the multiplicity cast into a more convenient form, by means of a logarithm. We define entropy as

$$S = k_B \ln \Omega. \quad (9.7)$$

The factor of Boltzmann's constant plays little role here, apart from giving entropy units (which are J/K).⁶ The logarithm is a monotonic function, which means that the larger Ω gets, the larger S gets. So being the most probable state is the same as being the highest entropy state. This is a really important statement, so important that we will elevate it to box-dom:

Entropy is a measure of probability: the more probable a state, the higher its entropy.

Entropy is often incorrectly described as a measure of the disorder of a system. This is simply not true; entropy is measure of probability and probability only. It **is** true that higher entropy states are often more disordered than lower-entropy states, but this is not always true; there are many examples of systems that become **more** ordered as their entropy increases.

We can now write the second law of thermodynamics rather concisely as a statement of probability, given in the boxed statement at the end of the previous section:

$$\Delta S_{\text{total}} \geq 0. \quad (\text{Entropic version of 2nd law}) \quad (9.8)$$

Starting from some initial state that is not the maximum entropy state, the combination of all our subsystems will exchange thermal energy and move spontaneously toward the maximum entropy state. And for large systems, it moves irreversibly: there is a negligibly small probability of moving away from the maximum entropy state (think about the sharply peaked multiplicity).

⁶By the way, Boltzmann was the one who realized that the second law had a probabilistic origin, and Eq. (9.7) is engraved on his tombstone. Check it out if you're ever in Vienna.

Note that the entropic form of the second law refers to the **total** entropy of a system, i.e., the **total** entropy cannot decrease. But the entropy of part of a system **can** decrease. So, for instance, it is very possible to have a chemical reaction where the stuff inside your beaker ends up with a lower entropy, as long as there is a corresponding increase in entropy somewhere else (most likely in the air around the beaker whose entropy increases when heated up by heat flowing from the beaker).

We could have expressed all this with the multiplicity, so why take a logarithm and call it entropy? There are three reasons. First, since multiplicities become very, very large for even modest sized systems, we find more workable expressions if we use the logarithm. For example, in the previous case of 100 oscillators with 200 energy units, we get an entropy of

$$S/k_B = \ln \Omega = \ln \left(\frac{299!}{200! 99!} \right) = 190, \quad (9.9)$$

which is much nicer to manipulate and plot than 10^{82} .

The second reason is that the combined entropy of two systems is simply the sum,

$$S_{AB} = S_A + S_B, \quad (9.10)$$

which you will show in Problem 14. When we are trying to identify the maximum entropy state, we can combine the contributions S_A and S_B from subsystems A and B by simply adding them together (like we would for energies). That will turn out to be handy now as we finally come to the definition of temperature.

The third reason is historical: it so happens that entropy was defined by Clausius a few years before Boltzmann developed a probabilistic theory for thermodynamics. Clausius defined the quantity that he called *entropy*⁷ in terms of energy flow in a thermodynamical system (to be discussed in the next chapter). He even stated the entropic form of the second law of thermodynamics, though no one at the time understood that this is really a statement of probability. So, taking the logarithm of multiplicity was needed to keep the entropic statement of the second law consistent with that proposed by Clausius.

9.6 The Definition of Temperature

As we discussed in Chapter 6, temperature is often defined in terms of the thermal kinetic energy. Certainly thermal kinetic energy and temperature are related, via the equipartition theorem, so it is a useful and convenient

⁷Clausius chose the word *entropy* partially after the Greek word *trope* which means *transformation* and partially because he wanted a word that sounded similar to *energy* since he defined entropy in terms of an energy flow.

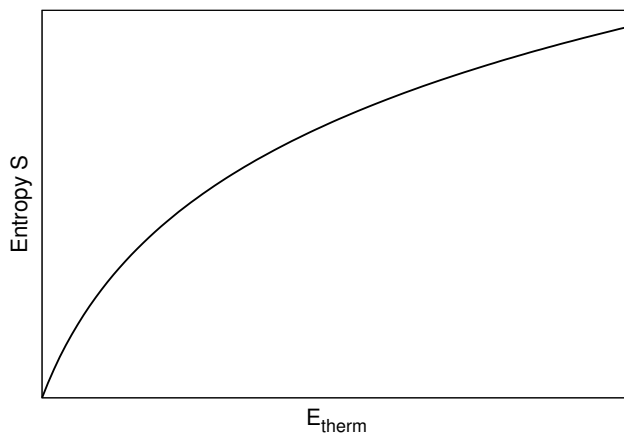


Figure 9.4: Entropy as a function of thermal energy.

picture to have. But defining temperature this way leaves its most fundamental role — namely, that it is the traffic cop dictating which way thermal energy will spontaneously flow — completely unexplained. In this section we will introduce a definition of temperature that naturally explains its presence in the Clausius statement of the second law. Conveniently, this *second law temperature* turns out to be the same temperature we know and love from the ideal gas law, the equipartition theorem, and the ball-spring solid.

Let's think of the entropy of a system as a function of its thermal energy. Adding more thermal energy to a system gives more ways to distribute the energy, and so increases the multiplicity. This means an increase in entropy, so S should be an increasing function of E_{therm} . A typical dependence of entropy on E_{therm} is shown in Fig. 9.4. Note that the entropy is increasing with E_{therm} , but also note that the rate of increase slows down with increasing energy. That is, the slope is steadily decreasing as E_{therm} increases. This can be understood as a type of diminishing returns: systems with very low E_{therm} can gain a lot of multiplicity by adding energy. Once the thermal energy is high, additional thermal energy has less impact on the entropy.

Now let's couple two subsystems, A and B . The combined energy is fixed, $E_{\text{total}} = E_A + E_B$. Consequently, as system A gains energy, system B loses energy, and vice-versa. In Fig. 9.5 we plot both S_A and S_B , but notice that the S_B curve is flipped over left to right. This is because $E_B = 0$ occurs at the right side of the plot, where E_A is at its maximum, and E_B increases as you move to the left. The reason for plotting it this way is that we can, for a particular choice of E_A , read off both $S_A(E_A)$ and $S_B(E_B)$. Also shown on the plot is the combined entropy $S_{\text{total}} = S_A + S_B$.

Now imagine starting with a relatively small value of E_A , where the

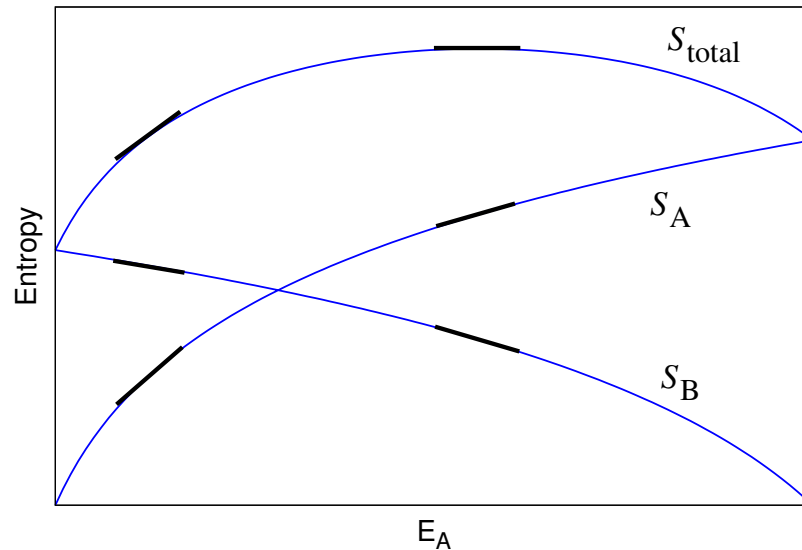


Figure 9.5: Entropies of subsystems A and B , as well as the combined system entropy S_{total} , all plotted versus E_A .

heavy lines are drawn on the left. What would be the net effect on the entropy if we were to take some energy from system B and give it system A ? The plot shows that S_B would decrease and S_A would increase. The plot also shows that, since the S_A curve in this region is steeper than the S_B curve, system A would gain more entropy than system B would lose. In other words, S_{total} would increase. Therefore, the “force” of probability pushing towards a (vastly) more probable state dictates that energy flows from system B to system A .

What the previous analysis should make clear is that the question of which way the energy will flow is determined by the magnitude of the *slope* on an entropy versus energy graph. Whichever system, A or B , has the steeper slope will be the one to receive the energy.

Let’s carry this analysis further. After some energy has flowed from A to B , we find that E_A has increased to where the second set of heavy lines are drawn. Here, the slopes of the S_A and S_B curves are equal in magnitude and opposite in sign. Any entropy change of system A is canceled by the entropy change of system B , so there is no longer entropy gained by increasing E_A (or decreasing it). Thermal energy will no longer be transferred because we are at the maximum combined entropy, which can be seen from the plot of S_{total} , and we have reached thermal equilibrium. Any additional transfer of energy (in either direction) will result in a decrease in total entropy.

All this discussion leads to the notion that the slope dS/dE_{therm} is direct-

ing the thermal energy traffic. Whichever subsystem has the smaller slope will give up energy to the subsystem which has the larger slope. Hence, we define temperature as

$$\frac{1}{T} \equiv \frac{dS}{dE_{\text{therm}}}, \quad (9.11)$$

and our probability analysis becomes equivalent to the Clausius statement.

This definition, then, explains the role of temperature in the second law, but does it match our previous notions of temperature? And what does it mean intuitively? First, yes, it does match the ideal gas temperature, etc. This can be shown by deriving the equipartition theorem from this definition of temperature; all our previous uses for temperature (such as the ideal gas) had their origin in the equipartition theorem.

As for an intuitive meaning, think of it this way: inverse temperature (that is, $1/T$) is a measure of how much use a system has for energy. When a system can find many ways to divide up the energy, then adding some energy will increase S a lot. That is a low temperature system. A high temperature system is one where diminishing returns has set in, and additional energy does not result in a substantial entropy increase.

Finally, note that for large systems we can add some amount of energy without significantly changing the temperature (for example, adding 10 joules of thermal energy to a cup of water). In this case, we can approximate Eq. (9.11) as

$$\frac{1}{T} \approx \frac{\Delta S}{\Delta E_{\text{therm}}} \quad \text{or} \quad T \approx \frac{\Delta E_{\text{therm}}}{\Delta S}. \quad (9.12)$$

This is often a handy way to *estimate* temperature from entropy change or vice-versa. **IMPORTANT NOTE:** use Eq. (9.12) **only** if ΔS and ΔE_{therm} are small. If you are given the entropy S as a function of E_{therm} , you should be using Eq. (9.11).

Example 9.3 The Temperature of my Coffee

Adding 50 J of thermal energy to my coffee cup caused its entropy to increase by an amount of 0.17 J/K. Estimate the temperature of my coffee.

Solution: According to Eq. (9.12) we have

$$T \approx \frac{\Delta E_{\text{therm}}}{\Delta S} = \frac{50 \text{ J}}{0.17 \text{ J/K}} = 294 \text{ K}. \quad (9.13)$$

That's room temperature. Yuck!

Problems

1. Consider an Einstein solid with three oscillators and four units of energy.
 - (a) Calculate the multiplicity for this macrostate.
 - (b) Write out the triplet for each possible microstate. For example, the microstate where the first oscillator has all the units of energy can be written as $(4, 0, 0)$. Confirm that you find the correct number of microstates.
2. Calculate the multiplicity of an Einstein solid with 24 oscillators and 15 energy units.
3. Suppose you roll a fair six-sided die three times in a row.
 - (a) Determine the probability of getting exactly the sequence 1–3–2?
 - (b) Now determine the probability of getting any other particular sequence (hint: no calculation necessary).
 - (c) What is the probability of rolling a sum of 6?
4. For two Einstein solids with $N_A = 3$ and $N_B = 3$ and six energy units, how many times more probable is the macrostate with equally shared energy than the macrostate where system A has all the energy? Use Table 9.2.
5. 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. Explain why this statement is more accurate for large systems than for small systems.
6. A large object's entropy is observed to increase by 0.15 J/K when we add 45 J of thermal energy. Assume that this causes a negligible increase in the temperature of the object. Determine the approximate temperature of the object.
7. The idea of “diminishing returns” says that while the entropy does increase with increasing thermal energy, the slope is decreasing (see Fig. 9.4). The Einstein solid multiplicity, like most materials, shows this behavior. Here is how to see it:
 - (a) For an Einstein solid with 10 oscillators and 5 energy units, calculate how much the entropy increases, i.e. ΔS , if you add one more energy unit (you may leave your answer in terms of k_B).

- (b) Now consider an Einstein solid with 10 oscillators and 15 energy units, and calculate how much the entropy increases if you add one more energy unit.
- (c) Do your answers to (a) and (b) confirm the diminishing returns? Explain why.

8. For two Einstein solids A and B , the entropy as a function of thermal energy is given by

$$S_A = k_B 400 \ln(E_A/300) \quad S_B = k_B 100 \ln(E_B/800)$$

where E_A and E_B are the thermal energies of systems A and B . If the two solids are brought to thermal equilibrium, what relation, if any, can be made between the final energies $E_{A,f}$ and $E_{B,f}$?

9. Consider a very strange system whose multiplicity is $\Omega_A = 1$ regardless of how much energy it has. Imagine starting this system with some amount of energy and bringing it into thermal contact with system B , an Einstein solid.

- (a) In which direction will the energy flow, or will no energy flow?
- (b) What can you say about the energies of the final state? For example, will they be equal? If they are unequal, which is larger? Is there anything more you can conclude?

10. A substance has entropy $S = c\sqrt{E_{\text{therm}}}$, where c is some constant. Use the definition of temperature to find E_{therm} as a function of T .

11. Consider two Einstein solids with $N_A = 3$ and $N_B = 3$ and eight energy units.

- (a) Make a table like Table 9.2. Note that many of the multiplicities you will need are already in Table 9.2, so there is no need to re-calculate everything.
- (b) How many times more probable is the macrostate with equally shared energy than the macrostate where system A has all the energy?

12. An Einstein solid has four oscillators and three units of energy.

- (a) Calculate the multiplicity of the solid.
- (b) Identify all the possible microstates using the parenthesis notation of Example 1.

13. System A and system B are both large. For system A , adding 250 J of thermal energy causes an entropy increase of 0.80 J/K. For system B , adding 250 J of thermal energy causes an entropy increase of 0.60 J/K.
- (a) Without mentioning temperature, use probability arguments to determine which way thermal energy will flow when systems A and B are thermally coupled.
 - (b) Estimate the temperature of each object and check that your result is consistent with part (a).
14. Show that $S_{AB} = S_A + S_B$ follows from the definition of entropy.
15. Entropy applies to more than just heat flow. We can use entropy and the second law of thermodynamics to discuss movement of air in a room.
- (a) Consider a room with only 100 gas molecules. Theoretically, the gas molecules can move anywhere in the room. Calculate the probability that all 100 of the molecules will be found on one particular side of the room.
 - (b) Now, consider a real room with a realistic amount of gas in it – let's say that there are 10^{26} gas molecules in the room. Calculate the probability that all of these gas molecules will be found in one particular side of the room. (Note: the probability is **so** small that your calculator or computer might simply give “0” for the answer.)
 - (c) Is it reasonable to say that you will “never” find all the air in one side of the room?
 - (d) Now, write a couple of sentences explaining why it is (from a probability perspective) that when a perfume bottle is opened, the scent of the perfume will spread throughout the room.
 - (e) After the perfume smell has spread throughout the room, would you expect all of the perfume molecules to go back into the bottle? Discuss this using the entropic form of the second law of thermodynamics.

16. The graphs in the figure below give plots of entropy S vs. E_{therm} for two different solids, A and B. Solid A starts with indicated energy E_A and entropy S_A , and Solid B starts with E_B and S_B . When Solid A has energy E_A , the slope of the entropy vs. energy curve is $dS_A/dE = 0.2 \text{ K}^{-1}$, and when Solid B has energy E_B , the slope of the entropy vs. energy curve is $dS_B/dE = 0.4 \text{ K}^{-1}$.

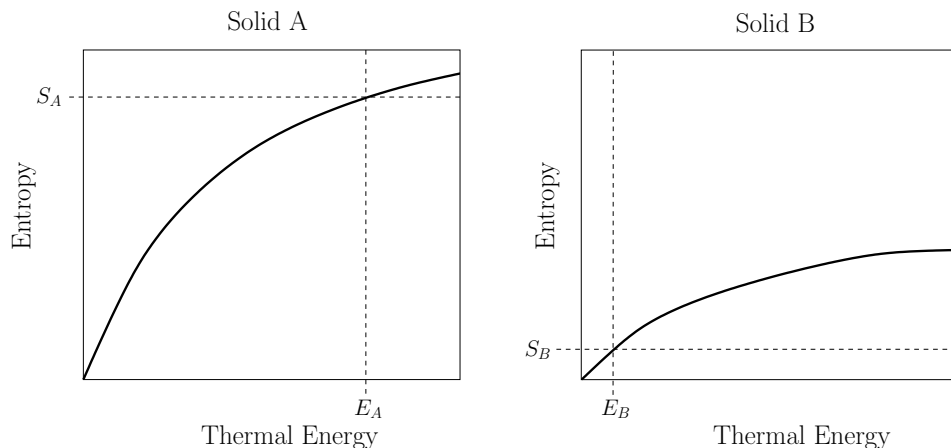


Figure 9.6: Figure for Problem 16

The two solids are brought into thermal contact with each other so that energy can flow between them.

- Which way will the energy flow: from A to B, from B to A, or will no energy flow? Give qualitative reasoning to support your answer.
- Now let's get quantitative. Calculate the approximate entropy changes ΔS_A and ΔS_B , and ΔS_{total} if 3 J of energy flow between the two solids in the direction that you chose in part (a).
- By what factor has the multiplicity for the total system increased from this energy transfer? In other words, calculate the ratio of multiplicities $\Omega_{\text{after}}/\Omega_{\text{before}}$.

Note: The answer you get will be a ridiculously, mind-boggling, impossible-to-put-into-words-just-how-huge-it-really-is number that you will not be able to calculate — you'll have to express it as $e^{\text{something really big}}$. To give you an idea of just how large this number is, if you were to write it as a digit followed by a bunch of zeros, and if each digit were 5 mm wide, the number would fill up several *light years*.

- Explain in your own words why heat flows in this system when the two solids are brought into contact. Don't use the words "entropy" or "second law" but rather explain it based on probabilities.

17. The graphs in the figure below give plots of entropy S vs. E_{therm} for two different solids, A and B. Solid A starts with indicated energy E_A and entropy S_A , and Solid B starts with E_B and S_B . When Solid A has energy E_A , the slope of the entropy vs. energy curve is $dS_A/dE = 0.5 \text{ K}^{-1}$, and when Solid B has energy E_B , the slope of the entropy vs. energy curve is $dS_B/dE = 0.1 \text{ K}^{-1}$.

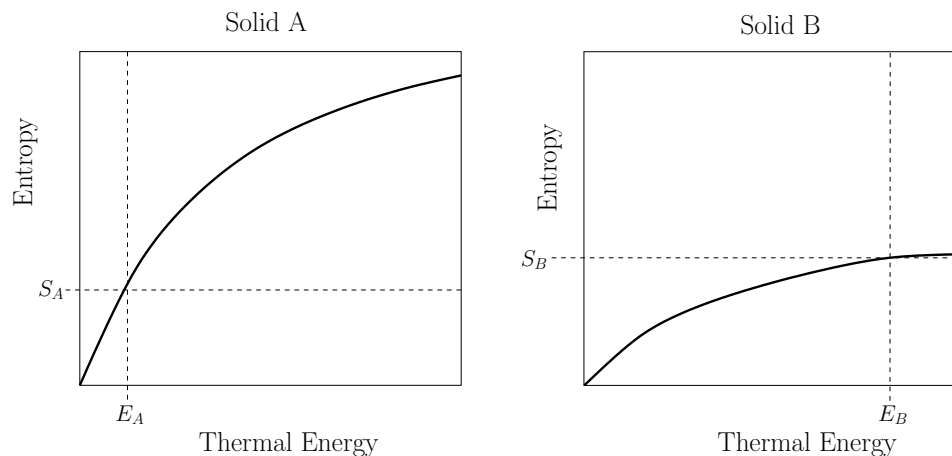


Figure 9.7: Figure for Problem 17

The two solids are brought into thermal contact with each other so that energy can flow between them.

- Which way will the energy flow: from A to B, from B to A, or will no energy flow? Give qualitative reasoning to support your answer.
- Now let's get quantitative. Calculate the approximate entropy changes ΔS_A and ΔS_B , and ΔS_{total} if 2 J of energy flow between the two solids in the direction that you chose in part (a).
- By what factor has the multiplicity for the total system increased from this energy transfer? In other words, calculate the ratio of multiplicities $\Omega_{\text{after}}/\Omega_{\text{before}}$.

Note: The answer you get will be a ridiculously, mind-boggling, impossible-to-put-into-words-just-how-huge-it-really-is number that you will not be able to calculate — you'll have to express it as $e^{\text{something really big}}$. To give you an idea of just how large this number is, if you were to write it as a digit followed by a bunch of zeros, and if each digit were 5 mm wide, the number would fill up several *light years*.

- Explain in your own words why heat flows in this system when the two solids are brought into contact. Don't use the words "entropy" or "second law" but rather explain it based on probabilities.

18. System A and System B are brought into thermal contact when the energy in A is $E_A = 1000$ J and the energy in B is $E_B = 1100$ J. Using the table below, listing energies and corresponding entropies of the two systems, determine whether heat will flow from A to B, or from B to A. Show all your work.

E_A (J)	E_B (J)	S_A (J/K)	S_B (J/K)
950	1150	6.76	10.34
975	1125	6.84	10.21
1000	1100	6.93	10.08
1025	1075	7.02	9.95
1050	1050	7.10	9.82

