Physics 3700

Microstates and Macrostates. Multiplicities. The Second Law.

Relevant sections in text: §2.2 – 2.5

Microstates and Macrostates

What is thermal equilibrium? What is temperature? Why does heat transfer energy from higher to lower temperatures? One cannot get very far with such questions in traditional thermodynamics because thermal equilibrium, heat and temperature are more or less defined via the laws of thermodynamics. We have introduced the concepts of temperature and heat via the zeroth and first laws. Our next subject will be the second law, which characterizes (among other things) heat transfer of energy and relaxation to equilibrium. To understand the origins and meaning of the second law it is instructive to take a pretty general look at the microscopic statistical behavior of a macroscopic system. This leads to a number of payoffs: a better understanding of the idea of temperature and heat, plus a new, very profound observable: the entropy.* This is what we will do now.

By analyzing the microscopic structure of systems to understand their thermodynamic behavior, we are going beyond traditional thermodynamics. The realm we are entering is sometimes called *statistical thermodynamics.*

We first introduce the very fundamental statistical ideas of *microstates* and *macrostates.* Given a system (*e.g.,* a gas), we view it as built from some elementary constituents, (*e.g.,* molecules). Each constituent has a set of possible states it can be in. The thermodynamic state of the system (which characterizes the values of macroscopic observables such as energy, pressure, volume, *etc.*) corresponds to many possible states of the constituents (the molecules). The collection of states of all the constituents is the *microstate.* To keep things clear, we refer to the macroscopic, thermodynamic state as the *macrostate.* The vast disparity between the number of possible macrostates versus microstates is at the heart of thermodynamic behavior! The number of distinct microstates giving the same macrostate is called the *multiplicity* of the macrostate. The multiplicity is a sort of microscopic observable which can be assigned to a macrostate.

Here's an elementary example. Consider what happens when you roll a pair of dice. Think of the 2 dice together as playing the role of the macroscopic system, and let the individual dice play the role of the microscopic constituents. Then the two individual dice values be the microstate and the total value of the dice roll defines the macrostate. There

---

* The entropy can be defined as a thermodynamic observable with no reference to an underlying statistical model, but it is much more instructive to derive it from microscopic considerations.

are 11 macrostates: (2, 3, 4, ..., 11, 12). Let us compute the multiplicities of each of these macrostate. We display them as pairs:

$$\text{(macrostate, multiplicity)} = \\ (2,1),(3,2),(4,3),(5,4),(6,5),(7,6),(8,5),(9,4),(10,3),(11,2),(12,1).$$

By the way, you can see the *relative probabilities* for various dice rolls here, assuming that each microstate is equally likely. For example, it is $6/2 = 3$ times more likely to roll a seven than to roll a 3. To get the actual probabilities of a given macrostate you have to figure out the probability for an individual microstate – always 1/36 in the dice example – then multiply by the multiplicity.* So, for example, the probability of rolling a 4 is $3/36 = 1/12$. (Note that the mulitiplicities add up to 36, so that the probability for getting anything between 2 and 12 is $1/36 + 2/36 + \cdots + 1/36 = 1$.)

In the dice example, there were 2 constituents and each constituent had 6 possible states, leading to $6 \times 6 = 6^2 = 36$ possible microstates. Macroscopic systems have many constituents so we should explore what happens when there are many constituents. If there are N constituents, and each has p states, then there are p^N possible microstates. This number can be enormous. Already for 2 dice we had 36 microstates. The number of macrostates is smaller — much smaller for large N — than the number of microstates. For the dice we had 11 macrostates. For three dice we have $6^3 = 216$ microstates and 16 macrostates.

As another example, suppose you had N coins. These are the constituents of your system and each has two possible states: heads (H) and tails (T). There are 2^N possible microstates. If a macrostate is specified by the number of heads and tails, how many macrostates are there? Well, first of all, you must note that if there are N_H heads, then there will be $N - N_H$ tails, so we only need to see how many possible values there are for N_H.† This is $N+1$, as you can easily see. What are the multiplicities of these macrostates? How many ways can you arrange N_H heads among N coins? We are trying to pick N_H coins to be heads out of N total coins – how many ways to choose N_H objects out of N objects? This is a fundamental question from combinatorics. The answer is given by the binomial coefficient $\binom{N}{N_H}$.

In case you don't know this or recall it, the binomial coefficient $\binom{n}{m}$, spoken of as "n choose m", is given by (with $n \geq m$):

$$\binom{n}{m} = \frac{n!}{m!(n-m)!}.$$

---

* Equivalently, divide the multiplicity by the total number of microstates.

† By the way, if you view this macroscopic system as having only the two observables, N_H and N_T, then the dimensionality of the system is unity, since measuring either of the observables determines the (macro)state.

This is the number of distinct ways of choosing m objects from a collection of n objects. (Note that this formula passes some simple sanity checks: When $m = n$, we have $\binom{n}{n} = 1$; when $m = 1$ we get $\binom{n}{1} = n$. Try some other simple examples.) The binomial coefficient can often be used to compute multiplicities - you just have to find a way to formulate the counting problem as choosing m objects from n objects. Sometimes this takes some ingenuity.

Anyway, the multiplicity of a macrostate of N coins with N_H heads and $N_T = N - N_H$ tails is given by

$$\binom{N}{N_H} = \frac{N!}{N_H!(N-N_H)!} = \frac{N!}{N_H!N_T!}.$$

Since the total number of microstates is 2^N we see that the probability $P(N_H)$ for getting N_H heads is

$$P(N_H) = 2^{-N}\frac{N!}{N_H!N_T!}.$$

Quantum Paramagnet

This same sort of counting can be used to compute the multiplicities of macrostates in an elementary (quantum!) model of a paramagnet. We can view the paramagnet as N magnetic moments each of which can be in 2 states – either pointing parallel or anti-parallel to some given axis (determined, *e.g.,* by an applied magnetic field). These states are referred to as "up" and "down", respectively. The total magnetization M along the given axis of the paramagnet is then proportional to the difference $N_{up} - N_{down} = 2N_{up} - N$. Evidently, the macrostate specified by M has multiplicity Ω given by the number of ways of choosing N_{up} magnetic moments to be "up" out of a total of N magnetic moments. We have

$$\Omega = \binom{N}{N_{up}}.$$

Paramagnetism is like coin tosses!

Einstein Solid

As a last, but important, example of microstates, macrostates and multiplicities, let us consider the *Einstein model for a solid.* We will use this simple model to make our first attack on the microscopic meaning of temperature and heat. The Einstein model of a solid will, like the ideal gas, be a standard example for many subsequent ideas.

The model amounts to viewing a solid as a collection of identical three-dimensional oscillators. Each three-dimensional oscillator can be viewed as 3 one-dimensional oscillators. Thus the Einstein solid can be viewed as having N constituents, each of which is a 1-d oscillator (so the number of 3-d oscillators— atoms — is $N/3$.)*

As you may recall, quantum mechanical oscillators in one-dimension have energies $(n + \frac{1}{2})\hbar\omega$, $n = 0, 1, 2, \ldots$, where ω is the natural angular frequency of the oscillator. Note the difference in energies between adjacent states is always the same, $\hbar\omega$. Evidently, the (macroscopic) internal energy U ranges from the ground state energy $\frac{N}{2}\hbar\omega$ (the "zero point energy") to arbitrarily large values. If we measure energy relative to the ground state energy and divide it by $\hbar\omega$ we can characterize the energy of the solid by a non-negative integer

$$q = \frac{U - \frac{N\hbar\omega}{2}}{\hbar\omega}.$$

So, if all the oscillators are in their ground state — all the n's are zero — we have $q = 0$. If one oscillator is in its first excited state — one of the n's is unity, the rest are zero — we have $q = 1$, and so forth. As you can see, q counts how many units of energy $\hbar\omega$ have been added to the ground state energy (irrespective of how the energy is divided up among the oscillators).

We consider macrostates determined by the total energy of the system – all the oscillators; we keep all other observables fixed. Thus the macrostate of the solid is determined by q (if we just consider the energy observable). The microstates here are just an assignment of a value of n to each of the N oscillators. For given values of q and N, a simple argument developed in your text shows that the multiplicity $\Omega(N, q)$ of the macrostate is given by

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

To see how this works, let $N = 3$. If we choose $q = 0$ (all oscillators in their ground state), the multiplicity should be one. We have

$$\Omega(3, 0) = \binom{2}{0} = \frac{2!}{0!\,(2 - 0)!} = 1,$$

of course. If we choose $q = 1$, this corresponds to having 1 oscillator in its first excited state, and the other two oscillators in their ground state. We should have $\Omega(3, 1) = 3$, right? We do indeed have

$$\binom{3}{1} = \frac{3!}{1!\,2!} = 3.$$

---

* A better model of the solid uses the normal modes of the coupled oscillator system describing the motion of the atoms near equilibrium. These normal modes of vibration are, in the quantum domain, known as *phonons*. While we shall refer to Einstein's formulation of the model, whether we use phonons or atomic oscillators we get pretty much the same basic results (although the frequencies of the oscillators differ significantly in the two cases). Really what we are studying here is the statistical thermodynamics of a system of N oscillators.

More generally, for any N, when $q = 1$ we get $\Omega(N, 1) = N$, as you should expect. You can try some other examples.

Large numbers – using Stirling's approximation to compute multiplicities and probabilities

Thermodynamic behavior is a consequence of the fact that the number of constituents which make up a macroscopic system is very large. We need to get good at dealing with large numbers. Here is a nice, illustrative exercise (see Problem 2.16 in your text).

Suppose you have 2 coins and you flip them. Let the macrostate just be determined by, say, the number of heads which appear. What is the probability distribution for the macrostates? We could use the general formulas, but it is easy to compute this directly. There are $2^2 = 4$ possible microstates (HH, HT, TH, TT). The multiplicity of the macrostate with two heads is one, as is the multiplicity of the macrostate with 2 tails. The multiplicity of the macrostate in which one is heads the other tails is 2. The probability for two heads is the same as the probability for two tails: 1/4. The probability for a heads-tails macrostate is 1/2. So the heads-tails result is more likely, but not overwhelmingly so. You wouldn't be shocked if you flipped the coins and got two heads. The probability distribution can be expressed as

$$(\text{macrostate}, \text{probability}) = (2 \text{ heads}, \frac{1}{4}),\ (1 \text{ head}, \frac{1}{2}),\ (0 \text{ heads}, \frac{1}{4}).$$

We have already noted in the context of rolling dice that the macrostate with the largest multiplicity is the most probable outcome of a dice roll (lucky 7). We see that result here, also. As you might imagine, this is a general rule: if all microstates are equally likely, the most probable macrostate is the one with the highest multiplicity.

For a small number of microsystems, the probability distribution tends to be wide – a wide range of macrostates have appreciable and/or comparable probability. The situation changes dramatically when larger numbers come into play. Suppose you have 1000 coins and flip them (or, if you like, you have one coin and you flip it 1000 times). What is the probability $P(500)$ of getting exactly 500 heads and 500 tails? Assuming as usual that all microstates are equally probable, the probability is given by the multiplicity of the given macrostate divided by the total number of microstates. The total number of microstates is 2^{1000}. The multiplicity of the macrostate with 500 heads is

$$\Omega(500) = \binom{1000}{500} = \frac{1000!}{500!^2}.$$

Naive manipulation of such large numbers can quickly get out of hand. Here is a standard strategy. We estimate the factorials appearing in $\Omega(500)$ using *Stirling's approximation* in the form:

$$N! \approx N^N e^{-N} \sqrt{2\pi N}.$$

This approximation is more and more valid the larger N becomes — try it. Using this approximation, we have

$$\Omega(500) \approx \frac{2^{1000}}{\sqrt{500\pi}},$$

so that the probability is given by

$$P(500) = \frac{\Omega(500)}{2^{1000}} \approx \frac{1}{\sqrt{500\pi}} \approx .025.$$

This is not so large. It's not that easy to get exactly a 50-50 split. But it *is* very likely that the result is *nearly* 50-50. To see this, consider the probability $P(600)$ for 600 heads and 400 tails. A similar computation gives (try it!)

$$P(600) \approx 10^{-11}.$$

It is not too hard to study the multiplicity formula and deduce that the macrostate with 500 heads is in fact the most probable macrostate. Evidently, the probability distribution is sharply peaked about the most probable macrostate by virtue of the large numbers involved.

Just to be complete, here is another (less accurate) version of Sterling's approximation:

$$\ln(N!) \approx N \ln(N) - N.$$

We can compare it to our earlier, more accurate version by taking the logarithm:

$$\ln(N!) \approx N \ln(N) - N + \ln(\sqrt{2\pi N}).$$

Evidently, the simpler approximation is off by $\ln(\sqrt{2\pi N})$. If N is really large, then this term is negligible in the first approximation compared to N. The simpler (albeit less accurate) form of Sterling's approximation is usually employed when we are trying to approximate the logarithm of a large factorial.

Large numbers for Einstein Solids

Now we use our approximation methods to derive an approximate formula for the multiplicities of macrostates for the Einstein solid, valid for a macroscopic system. Once we have this formula under control, we will be ready to discuss the microscopic, statistical meaning of thermodynamic equilibrium, temperature and heat — at least in the context of this simple model of a solid.

We begin by assuming that both N and q are "large", as they should be for a macroscopic system. We write $N, q >> 1$. We then have, as you can easily see,

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

We're not done. For any macroscopic solid (with $N \sim 10^{23}$, say) the factorials are enormous since both N and q are much greater than 1. To get a handle on them we take a logarithm and use the simple form of Stirling's approximation,

$$\ln(n!) \approx n\ln(n) - n, \quad n >> 1,$$

to get

$$\begin{aligned}\ln\Omega(N,q) &\approx \ln[(q+N)!] - \ln(q!) - \ln(N!)\\ &\approx (q+N)\ln(q+N) - q\ln(q) - N\ln(N) \quad N, q >> 1.\end{aligned}$$

Next we assume that $q >> N$. This assumption can be interpreted as saying that most oscillator degrees of freedom are highly excited compared to the ground state. This will turn out to be a high temperature approximation.* To take advantage of this assumption we write

$$\ln(q+N) = \ln[q(1+\frac{N}{q})] = \ln(q) + \ln(1+\frac{N}{q}).$$

The Taylor series of the logarithm $\ln(1+x)$ about $x = 0$ is

$$\ln(1+x) \approx x \quad x << 1.$$

Identifying x with $\frac{N}{q}$ we then get

$$\ln(q+N) \approx \ln(q) + \frac{N}{q}, \quad q >> N >> 1.$$

Using this approximation in the multiplicity we have

$$\ln\Omega(N,q) \approx N\ln(\frac{q}{N}) + N + \frac{N^2}{q} \approx N\ln(\frac{q}{N}) + N, \quad q >> N >> 1.$$

In the last approximation we have neglected N^2/q compared to N. This is a good idea since

$$\frac{\frac{N^2}{q}}{N} = \frac{N}{q} << 1.$$

---

* High temperature is relative — here we do not necessarily mean core of the sun types of temperatures or anything like that. "High" means there is enough energy in the system such that the oscillators are behaving classically. A good estimate of the temperature needed is given by $kT >> \hbar\omega$. If atomic vibrational energies are estimated to have size about 10^{-2} eV, then "high temperature" means on the order of 10^2 K or greater, which includes room temperature.

Now take the exponential of each side to get

$$\Omega(N, q) \approx \left(\frac{qe}{N}\right)^N, \quad q >> N >> 1.$$

This is the expression for the multiplicity of an Einstein solid we shall use to understand heat and thermal equilibrium. This formula is valid for a macroscopic system ($N >> 1$) at "high" temperature ($q >> N$).

Interacting Einstein solids

With our macroscopic, high temperature approximation in place, we can now address the interaction of two such Einstein solids. The goal is to understand better the meaning of temperature and heat. We will take two Einstein solids as our system. The two solids will be "isolated"; they will not be allowed to exchange energy with the rest of the universe. On the other hand, the two solids will be in "thermal contact" — we allow them to exchange energy with each other. Our goal is to determine the most likely equilibrium state for the two solids and interpret this in terms of the macroscopic notions of temperature and heat.

Denote the two Einstein solids by A and B, each with macrostate determined by q_A and q_B. For simplicity, we initially assume the solids are identical in the sense that they have the same number of oscillators and the same frequency of oscillator vibrations. (We shall relax this assumption soon.) The solids are identical in structure, but the macrostate of each solid, determined by q_A or q_B, can be different. We will isolate the two solids from the rest of the universe so the total energy — determined by $q = q_A + q_B$ — is fixed, but the two solids can exchange energy thus changing the values of q_A and q_B. Our plan is to figure out what are the most likely values for q_A and q_B. The macrostate of the combined system is determined by q_A and q_B.

To this end, let's write down the multiplicity Ω of the macrostate of the combined system determined by $q = q_A + q_B$ for a given q_A and q_B. Assuming the interaction between the two solids is sufficiently weak, the multiplicity of the combined system is just the product of the individual multiplicities for the two solids:

$$\Omega \approx \left(\frac{q_A e}{N}\right)^N \left(\frac{q_B e}{N}\right)^N = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N, \quad q_A, q_B >> N >> 1.$$

Notice that the multiplicity of the macrostate depends upon the energies of the individual solids, q_A and q_B. We would now like to figure out for which values of q_A and q_B is the multiplicity for the combined sytem (just computed) the largest — this will evidently determine the most likely values for q_A and q_B. Since the number of constituents of each solid is so large, we expect that the system will have negligible probability to be in a state which differs appreciably from the most probable (highest multiplicity) state.

Keeping in mind that $q = q_A + q_B$ is fixed, this can be easily translated into a simple calculus problem: find the values of $x = q_A$ such that $f(x) = [x(q-x)]^N$ is maximized. First we must find the critical points of f, where the first derivative of f vanishes. We have

$$\frac{df}{dx} = N[x(q-x)]^{N-1}(q-2x).$$

This vanishes when $x = 0, q, q/2$. The first two cases correspond to a minimum of the function, the last gives the maximum. (You could also see this by computing the second derivative at the critical points.) So, given q, the multiplicity is largest when

$$q_A = q_B = \frac{q}{2},$$

i.e., the energy is equally shared between the (identical) solids. The maximum multiplicity is

$$\Omega_{max} \approx \left(\frac{eq}{2N}\right)^{2N}, \quad q >> N >> 1.$$

So — *assuming all microstates are equally likely (see below)* so we can use multiplicities to determine probabilities — if you allow the identical solids to exchange energy, the most likely outcome is that the one with less energy will gain energy from the one which has more energy so that the two end up with the same energy. Are there other possibilities? Sure. The energy of each solid and the energy per oscillator in each solid fluctuates, statistically speaking. But any result in which q_A is not very close to q_B is so unlikely as to be ignorable (recall the result with a very large number of coin tosses.) The idea of thermodynamics is to suppose that there are enough constituents to ignore all but the most likely result. Let us elaborate on this a little.

As shown in your text, in the vicinity of the maximum the multiplicity for the combined system is a *Gaussian.* The macrostate of the total system is determined by q_A. Setting

$$x = q_A - \frac{q}{2},$$

we have the multiplicity of the solid being given by

$$\Omega \approx \Omega_{max} e^{-N\left(\frac{2x}{q}\right)^2}, \quad |x| << q.$$

The Gaussian is peaked when $x = 0$ where $\Omega = \Omega_{max}$ (of course) and has a width† of $\frac{q}{2\sqrt{N}}$. Is this wide, narrow, or what? Well, first of all, notice that the order of magnitude of relevant q_A values is of order q. For $N \sim 10^{24}$ the width is of order $\frac{q}{10^{12}}$. The Gaussian is *very* narrow! (Just like in our coin toss example.)

---

† "Width" of a Gaussian is defined as the value of x such that the Gaussian has reaced $1/e$ of its maximum value.

What happens if the solids are of different "size", *i.e.,* have different numbers of oscillators? Let the number of oscillators be N_A and N_B with $N = N_A + N_B$. Now the multiplicity is

$$\Omega \approx \left(\frac{q_A e}{N_A}\right)^{N_A} \left(\frac{q_B e}{N_B}\right)^{N_B}.$$

You should try your calculus skills to see if you can find when this function is maximized as a function of q_A and q_B (keeping in mind that $q_A + q_B = q$ is fixed). You'll find

$$q_A = \frac{N_A}{N} q, \quad q_B = \frac{N_B}{N} q.$$

Assuming again that all microstates are equally likely (see below), this implies that the most probable situation is that

$$\frac{q_A}{N_A} = \frac{q_B}{N_B} = \frac{q}{N},$$

i.e., the energy per oscillator of both solids is the same — and is the same as the energy per oscillator of the composite system. As before, one can show that the multiplicity is a Gaussian which is very narrowly peaked about its maximum value. Note that this result includes our previous special case when $N_A = N_B$.

To summarize: For two macroscopic Einstein solids, characterized by a large number of microsystems and macroscopic energy (high temperature), the multiplicity is very sharply peaked about the configuration where the two sub-systems have the same energy per oscillator. As we let the number of constituents become arbitrarily large, the statistical fluctuations about this configuration become arbitrarily small. Notice that this result, which clearly illuminates heat and temperature, is a consequence of the fact that there are many constituents – we never had to commit ourselves to how they interact except to say that they can "exchange energy".

The fundamental assumption of statistical mechanics. The second law.

Now we are ready to use all this multiplicity mathematics to understand heat transfer and thermal equilibrium. Suppose we are given two macroscopic systems which are isolated from the rest of the universe, but are coupled so that they may exchange energy. We assume that the coupling is not so strong as to disturb the microsystem structure significantly (*e.g.,* they may be modeled as two Einstein solids exchanging energy). These assumptions are relatively minor. Our next assumption is significant; it is the Fundamental Assumption of Statistical Mechanics:

In an isolated system at thermal equilibrium, all microstates are equally likely.

The idea here is that *at the microscopic level*, transitions between states are reversible. For any two states, call them x and y, the probability for making a transition from $x \to y$ is the same as the probability for going from $y \to x$. This, principle – known as the "principle of detailed balance" – is born out by explicit computation in the framework of quantum mechanics, by the way. So, at the microscopic level it is reasonable to make the fundamental assumption. By the same token, it now becomes difficult to see where irreversible thermodynamic behavior comes from! Many processes in nature appear to only go in one direction – think of the free expansion of a gas. Of course, what distinguishes microscopic from macroscopic systems is the large numbers (*e.g.,* q and N) characterizing the constituents in the macroscopic case. Given the fundamental assumption above, we know that the (relative) probability distribution for macrostates is given by the multiplicities. And we have seen (at least in the Einstein solid example) how the multiplicity function is very sharply peaked about the state in which the two systems have the same energy per (oscillator) degree of freedom. In the Einstein solid example if, say, system A has all the energy initially, when equilibrium occurs it is overwhelmingly probable that systems A and B will have (nearly) the same energy per oscillator – the energy gets divided up evenly among all the oscillators. In light of the zeroth law, it is natural to associate the energy per degree of freedom with (some function of) the temperature — so that at equilibrium the temperature of both solids is the same. Note that this is *not* the statement that the energy of the solids is the same. The energies of the two solids are related by

$$\frac{q_A}{q_B} = \frac{N_A}{N_B}.$$

We have seen this before: the temperature of a system is more like "energy per degree of freedom" than "energy of the system".

We can view the fundamental postulate as, in effect, defining equilibrium microscopically in terms of equally probable microstates. Equally important, we now have arrived at a microscopic, statistical version of the **second law of thermodynamics**: *the state of an isolated thermodynamic system in equilibrium is the one with the greatest multiplicity.* In particular, we see that relaxation to equilibrium is a process in which multiplicity increases to its maximum value. This version of the law is very instructive, but – unlike the zeroth and first laws – it implicitly involves a microscopic description of the thermodynamic system (so one can talk about microstates and multiplicities). We will soon come up with a version of the second law which makes no reference to the microstructure of a system.

Notice that we included the term "isolated" in the fundamental assumption of statistical thermodynamics, and in the above statement of the second law. This means the system is *closed* and, in particular, its energy is fixed. The statistical description of macro/microstates of a closed system with fixed total energy (and volume and number of particles) is known as the *micro-canonical ensemble.* Here "ensemble" refers to the hypothetical large number of copies of the system which you could use to interpret probabilities in terms of frequencies.*

To summarize: using a microscopic description in terms of a very large number of constituents we have given statistical interpretation of the zeroth and first laws of thermodynamics, namely: Thermal equilibrium means that all microstates are equally likely. Energy in a closed system is conserved. And we have introduced a new law, the second law, in a statistical form: Equilibrium states maximize the multiplicity.

Multiplicity of the Ideal Gas

In the previous paragraphs I have drawn conclusions about generic thermodynamics systems based upon the Einstein solid example. This is all fine as far as it goes, but a single example is hardly compelling evidence for a general law. Let us look at another example and see how the same sort of behavior occurs.

We consider the multiplicities of macrostates of an ideal gas. This turns out to be technically a little less transparent than what we got by simple counting for the Einstein solid. You will see that the details are very different, yet the same sorts of conclusions about thermal equilibrium apply.

For simplicity we consider a monatomic gas (*e.g.,* Helium). The internal energy we consider is the total kinetic energy of the atoms. Suppose there are N atoms with mass m. Each atom has a particular 3-dimensional position and momentum, each given by 3 components. So, all together there are $3N$ position and $3N$ momentum components which we denote by x_i and p_i, $i = 1, 2, \ldots, 3N$. The (kinetic) internal energy is the sum of $3N$ one-dimensional kinetic energies:

$$U = \sum_{i=1}^{3N} \frac{1}{2m} p_i^2.$$

A macrostate is determined by specifying U and, say, the volume V (and N if we wish). The choice of V constrains the positions of the atoms. The choice of U constrains their momentum. The microstates are then an assignment of values to all the positions and momenta (x_i, p_i) of the atoms subject to these constraints.

We wish to compute the multiplicity of a state as a function of U and V (and N). What makes the analysis a little more tricky here is that the positions and momenta can vary continuously — naively it would appear that the multiplicity of any macrostate

---

* Later we shall encounter another kind of ensemble, the *canonical ensemble*, which corresponds to an open system in thermal equilibrium with an environment at a given temperature. Now the temperature is fixed instead of the energy, which undergoes (statistical) fluctuations.

should be infinite! Quantum mechanics and its uncertainty principle (which puts a limit on the resolution of volumes in position-momentum space) render the number of states finite. A hand-waving type of argument in the text establishes the following formula for the multiplicity:

$$\Omega(N,U,V) = \frac{1}{N!}\frac{V^N}{h^{3N}}\frac{2\pi^{\frac{3N}{2}}}{(\frac{3N}{2}-1)!}(2mU)^{\frac{3N-1}{2}}.$$

Here N is the number of atoms, U is the (kinetic) energy, h is Planck's constant, V is the volume of the gas. You might notice that we have introduced the factorial of a half-integer. This is defined by

$$(n+\frac{1}{2})! = \sqrt{\pi}\prod_{k=0}^{n}\frac{2k+1}{2},$$

where n is a non-negative integer. So, for example, if $n = 1$ we have

$$\frac{3}{2}! = \sqrt{\pi}(\frac{1}{2})(\frac{3}{2}) = \frac{3\sqrt{\pi}}{4}.$$

You should definitely read the argument leading to this expression for Ω in order to see what are the ingredients. We shall give a precise derivation of this formula much later, so I'll defer the discussion of the derivation. Instead, let's just see what the formula means. First and foremost, note that the multiplicity grows with increasing volume and with increasing energy. Let us see if we can understand the volume and energy dependence of this expression.

You can see that the multiplicity varies as the N^{th} power of the volume of the gas. To understand this, recall that the microstates are a specification of the position (and momentum) for each atom subject to the specification of the volume (and total energy). The positions can be anywhere in the given volume. So the multiplicity coming from possible positions for a single atom should be proportional to the volume, for two atoms it is proportional to the square of the volume, for 3 atoms it proportional to the cube of the volume, *etc.* . Another, fancier way to think about it is that specifying the positions of the atoms is the same as specifying a point in a space of $3N$ dimensions, where the volume of the space is V^N.

The energy factor comes from considering the possible ways the momentum can be divided up among the atoms, given the energy U. The energy condition defines a hypersphere(!) with dimension $3N-1$ and radius $\sqrt{2mU}$ in the $3N$ dimensional space of possible momentum at each location. The momentum contribution to the multiplicity should then be proportional to the hypervolume of this hypersphere. This (not surprisingly - think of the units) turns out to be proportional to the radius of the hypersphere raised to the $3N-1$ power, *i.e.,* $(2mU)^{\frac{3N-1}{2}} \approx (2mU)^{3N/2}$ when $N >> 1$. The multiplicity varies as the product of the energy and volume factors (as opposed to the sum, or the ratio or something else) because for a given position you can vary the momentum and vice versa.

Next we use the fact that N is large to simplify the expression for Ω:

$$\Omega(N,U,V) \approx \frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{\frac{3N}{2}}}{(\frac{3N}{2})!}(2mU)^{3N/2}, \quad N >> 1.$$

Thus Ω is of the form

$$\Omega \approx f(N)V^N U^{3N/2}, \quad N >> 1.$$

It is instructive to recall that the multiplicity of the Einstein solid with N atoms — $3N$ one-dimensional oscillators — and with energy defined by q was (for a large system at high enough temperature)

$$\Omega(N,q) \approx \left(\frac{eq}{3N}\right)^{3N},$$

The degrees of freedom for each oscillator in the Einstein solid (in the sense of equipartition) is $f = 6$.* So the energy dependence of the multiplicity for an Einstein solid is $U^{fN/2}$. The monatomic ideal gas we are considering here has $f = 3$ — corresponding to 3 translational degrees of freedom — so the energy dependence of the multiplicity is also $U^{fN/2}$. This energy dependence of the multiplicity is typical of any system obeying the equipartition of energy.

Finally I point out that the derivation of the multiplicity formula (see the text) assumes the particles are *indistinguishable*: there is no measurement which can tell which particle is which. All the atoms of the monatomic gas are intrinsically the same. This means that the microstate with a given particle, say, particle number 1 in (position, momentum) state $(\vec{x},\vec{p})$ and with particle 2 in the state $(\vec{x}',\vec{p}')$ is considered the same microstate as the one in which particle 1 in state $(\vec{x}',\vec{p}')$ and particle 2 in the state $(\vec{x},\vec{p})$. This reduces the multiplicity compared to the case where the particles are distinguishable in some fashion. As a humble illustration of this point, recall how we counted multiplicities for a pair of dice. There we treated the dice as *distinguishable* so that, for example, the multiplicity was 2 for a roll totaling 3. If the dice were *indistinguishable* then the multiplicity would be 1 for a roll of three.

Free expansion and . . . contraction

Here's a nice application of the volume dependence of the multiplicity for an ideal gas. It's a bit of a digression, but it's pretty neat. Suppose you have a container of volume V filled with an ideal gas in a state with temperature T and pressure P. The container is in

---

* We will explain equipartition in detail a little later. For now, the 6 degrees of freedom contribute to the energy according to 3 for the kinetic energy and 3 for the potential energy.

an insulated, empty room of size nV $(n > 1)$. If you open the container, you know what will happen. When equilibrium is again established the gas will fill the room. Note that no work or heat transfers took place; the process is called *free expansion.* (Can you see why $Q = 0 = W$ for this process?) Because the work and heat vanish, the energy of the gas doesn't change — this is from the first law. Thus a free expansion is an *isoenergetic* process. From $U = \frac{f}{2}NkT$, it follows that the process is isothermal — the temperature is still T at the new equilibrium.† The volume increased to nV and so, from the ideal gas law, the pressure decreased to P/n. So, to summarize, the free expansion of an isolated gas from volume V to, say, volume nV is a change of state characterized by

$$Q = 0 = W, \quad V \to nV, \quad P \to P/n, \quad T \to T.$$

The question I want to consider now is: can the reverse process occur? Can the gas undergo a "free contraction" from nV into a smaller volume V? In other words, can the gas be at equilibrium at volume V, temperature T and pressure P? The first law and ideal gas equations of state do not prohibit it. So why don't we ever see this happen? The reason is the very large number of microsystems, of course. Let's analyze the expansion/contraction scenario using our multiplicity function.

If there are N atoms in the gas the multiplicity for volume V is a factor of n^{-N} smaller than that for volume nV. At equilibrium at temperature T the value of U is the same, so the probability to be in the smaller container is n^{-N} times the probability to be in the larger container. Let us assume the room is twice as large as the container, $n = 2$. For starters, suppose there are 3 atoms.* The relative probability is 1/8. So it is less likely to find the atoms occupying the smaller volume (at equilibrium), but not dramatically so. Now suppose there are 100 atoms. Then the relative probability is $2^{-100} \approx 10^{-30}$ – very small! You'll agree that 100 atoms is hardly a macroscopic system. When the system is truly macroscopic, $N \sim 10^{23}$, the relative probability for the gas filling the container versus filling the room is essentially zero. This is why the free expansion of a gas is, for all practical purposes, not reversible. We say that the free expansion is *irreversible.* Contrast this with, for example, the quasi-static isothermal expansion/contraction of a gas in a cylinder which *is* a reversible process.

Two Interacting Ideal Gases.

Returning back to our main discussion, we consider two interacting identical ideal gases A and B. You can imagine that the two gases are in a box of volume $V = V_A + V_B$ which

---

† Note that this process should *not* be considered quasi-static. If you try to slowly enlarge the box until it fills the room, work will be done and the energy and temperature can change. This is fine, but it is not free expansion!

* Note that the derivation of the multiplicity formula (see text) reveals that the volume dependence of the multiplicity is not restricted by any large numbers approximation.

is partitioned into two volumes V_A and V_B by a wall which allows exchange of energy. We assume for simplicity that the gases are identical in the sense that m and N are the same for A and B. Let the total energy be $U = U_A + U_B$, which is held fixed – the system of two interacting gases is isolated from its environment. The multiplicity for a given U_A and U_B is then of the form

$$\Omega = \Omega_A \Omega_B = f(N)^2 (V_A V_B)^N (U_A U_B)^{3N/2}.$$

Let us study how the total multiplicity varies as a function of energy, volume, and number of particles. The variation of energy is just like that of the Einstein solid. We can then conclude that the multiplicity is sharply peaked in the vicinity of $U_A = U_B = U/2$ with width $\frac{U}{\sqrt{3N/2}}$. For large enough N, this width is small, of course. So, again we see that in thermal equilibrium it is overwhelmingly likely to find the gases to have the same energy per degree of freedom (and hence the same temperature).

Let us consider how the multiplicity varies with volume. You could imagine that the gases start off with some given initial energies and volumes and the partition is allowed to move as (mechanical and thermal) equilibrium is approached. The volume dependence is mathematically analogous to the energy dependence. It is sharply peaked when $V_A = V_B$ with width given by $V/\sqrt{N}$. So, again, for large N the width is small and it is almost certain that we'll find $V_A = V_B$ when equilibrium occurs.

Finally, one can consider what would happen if $N_A \neq N_B$. The analysis here is more complicated and I will spare you. But I will tell you the result: as with the Einstein solid, the equilibrium state – the state with the biggest multiplicity – is the one where the energy per degree of freedom is the same for both gases. This is, of course, just what we found with the Einstein solid and corresponds to the temperatures being equal at equilibrium. Similarly, the volume per degree of freedom is the same for both gases, which corresponds to the pressures being equal for both gases at equilibrium.

While two examples hardly prove anything in general, we see how the ideas of multiplicity and equal probabilities for microstates at equilibrium conspire with very large numbers of constituent microsystems to lead to familiar macroscopic results.