

# Entropy

## (Schroeder Chapter Two)

Physics A410\*

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# 1 Preamble

So far, we've looked at the role of energy (via first law of thermodynamics and the equipartition theorem) and the interrelationship among temperature, pressure, and volume (in the form of an equation of state such as the ideal gas law). Now we consider a new topic, the second law of thermodynamics, which explains why some processes, such as the flow of heat from high to low temperatures, occur spontaneously in one direction but not in the other. (This is actually kind of a deep question, since most of the fundamental laws of physics are time-reversal invariant. The source of the “thermodynamic arrow of time”, defined by the spontaneous flow of heat or more generally by the tendency of the total entropy of the universe to increase, needs to be explained.)

We'll see that what's actually happening is that violations of the second law aren't impossible, just phenomenally *unlikely*, and the underlying reason will be that for a broad description of a macroscopic system with a few variables ( $P, T, U$ , etc.), most of the details of the microscopic motion ( $\vec{r}_1, \vec{v}_1, \vec{r}_2, \vec{v}_2, \dots, \vec{r}_N, \vec{v}_N$ ) are irrelevant. This is a good thing, because for a typical macroscopic system  $N \sim 10^{23}$ .

## 2 Counting States

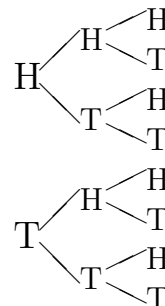
*In conjunction with this topic, you should read Sections 2.1 and 2.2 of Schroeder.*

We refer to a description of the system in terms of its macroscopic properties as a *macrostate*. If the macroscopic variables are the same for two systems, they are in the same macrostate, even if some of the microscopic details are different. The *microstate* of a system is the detailed description of every little piece of the system. In general, a system in a given macrostate can be in any of many many microstates. The number of microstates corresponding to a macrostate is called its *multiplicity*, which we traditionally write as  $\Omega$ .

### 2.1 Example: Two-State Systems

We can make these definitions more concrete with a simple idea, counting up the number of possible outcomes when tossing a bunch of coins.

- Toss one coin: there are 2 possible outcomes: heads (H) and tails (T)
- Toss two coins: there are  $2 \times 2 = 4$  possible outcomes (if we keep track of which coin is which: HH, HT, TH, and TT).
- Toss three coins: there are  $2 \times 2 \times 2 = 8$  possible outcomes:



- Toss  $N$  coins: there are  $\underbrace{2 \times 2 \times \dots \times 2}_N = 2^N$  possible outcomes.

For this system, each possible sequence of heads and tails is a different *microstate*; there are  $2^N$  microstates. The different *macrostates* are labelled by the total number of heads and tails.

For example, if  $N = 2$ , the microstates and their corresponding macrostates are

$$\text{HH} \quad 2\text{H} \quad \Omega(2\text{H},0\text{T}) = 1$$

$$\begin{array}{l} \text{HT} \\ \text{TH} \end{array} \quad 1\text{H} \quad \Omega(1\text{H},1\text{T}) = 2$$

$$\text{TT} \quad 0\text{H} \quad \Omega(0\text{H},2\text{T}) = 1$$

The macrostate with one head and one tail corresponds to two different microstates and therefore has a multiplicity of 2.

It's also useful to call the total number of microstates (which is the sum of the multiplicities of all the macrostates)  $\Omega(\text{all})$ . In this case,  $\Omega(\text{all}) = 2^N = 4$ .

Now, if the coin is fair, each microstate is equally probably, so the odds of getting  $n$  heads in  $N$  tosses are

$$\frac{\Omega(n\text{H}, [N - n]\text{T})}{\Omega_{\text{all}}} \tag{2.1}$$

The multiplicity  $\Omega(n\text{H}, [N - n]\text{T})$  can also be called  $\Omega(N, n)$  for short. Again, in the example of  $N = 2$ , the probabilities are

$$\begin{array}{ll} 2\text{H}, 0\text{T} & \text{odds} = \frac{1}{4} = 25\% \\ 1\text{H}, 1\text{T} & \text{odds} = \frac{2}{4} = 50\% \\ 0\text{H}, 2\text{T} & \text{odds} = \frac{1}{4} = 25\% \end{array}$$

To figure out  $\Omega(N, n)$  in general, we need to count the number of ways to pick  $n$  coins out of  $N$  to land heads up.

- If  $n = 0$ , there's only one way for all the coins to be tails up, so  $\Omega(N, 0) = 1$ .
- If  $n = 1$ , we can pick any of the  $N$  coins to be the one that's heads up, so  $\Omega(N, 1) = N$ .
- Now consider  $n = 2$ . There are  $N$  choices for the first coin and  $N - 1$  for the second. But we could have chosen the same two coins in either order, and we don't want to count for example #2 and #5 being heads-up as a different microstate than #5 and #2. So we need to divide by 2 to avoid double-counting:

$$\Omega(N, 2) = \frac{N(N - 1)}{2} \tag{2.2}$$

- Look at one more specific case,  $n = 3$ . We have  $N$  choices for the first heads-up coin,  $n - 1$  for the second and  $n - 2$  for the third. But there are  $3 \times 2 = 6$  different orders in which the same three coins could be picked. So

$$\Omega(N, 2) = \frac{N \cdot (N - 1) \cdot (N - 2)}{3 \cdot 2} \tag{2.3}$$

- In the general case, we have  $N \cdot (N - 1) \cdot \dots \cdot (N - n + 1)$  ways of picking  $n$  coins, but  $n \cdot (n - 1) \cdot \dots \cdot 2$  different orders in which the same  $n$  coins could be picked, so

$$\Omega(N, n) = \frac{N \cdot (N - 1) \cdot \dots \cdot (N - n + 1)}{n \cdot (n - 1) \cdot \dots \cdot 2} \quad (2.4)$$

We can write this more compactly by using a new notation. The factorial of  $n$ , written  $n!$  and pronounced “ $n$ -factorial”, is the product of all positive integers up to  $n$ . [Note that by definition  $0! = 1$ , which ensures that  $(n + 1)! = (n + 1)n!$  for any non-negative integer  $n$ .] This is written

$$n! = 1 \cdot 2 \cdot 3 \cdot \dots \cdot (n - 1) \cdot n \quad (2.5)$$

which is just the denominator of our multiplicity:

$$\Omega(N, n) = \frac{N \cdot (N - 1) \cdot \dots \cdot (N - n + 1)}{n!} \quad (2.6)$$

Now, the numerator is not quite  $N!$  because it doesn’t go all the way down to 1:

$$N! = N \cdot (N - 1) \cdot \dots \cdot (N - n + 1) \cdot \underbrace{(N - n) \cdot (N - n - 1) \cdot \dots \cdot 2 \cdot 1}_{\text{missing part}=(N-n)!} \cdot \quad (2.7)$$

So

$$\frac{N!}{(N - n)!} = N \cdot (N - 1) \cdot \dots \cdot (N - n + 1) \quad (2.8)$$

which means

$$\Omega(N, n) = \frac{N!}{n!(N - n)!} \quad (2.9)$$

In fact, this combination of factors, the number of different ways of choosing  $n$  objects out of  $N$ , is so common that it has its own notation

$$\binom{N}{n} = \frac{N!}{n!(N - n)!} \quad (2.10)$$

which is pronounced “ $N$  choose  $n$ ”.

The coin-flipping example seems kind of artificial, but as Schroeder describes, it’s actually applicable to a system called a 2-state paramagnet. We’ll look at that system more later on, but for now, let’s turn to a physically more interesting “toy model”.

## 2.2 The Einstein Model of a Solid

This toy model, which Schroeder uses to develop a lot of the statistical underpinnings of thermodynamics, is called the *Einstein solid*. This models a solid as a system of  $N$  harmonic oscillators. The physical picture is that each atom sits at a position in a crystal lattice, but it can vibrate about that location in three dimensions, and those oscillations can be

approximated as simple harmonic motion. Note that this means each atom corresponds to *three* harmonic oscillators,<sup>1</sup> one in each direction, which we can see from the potential energy

$$V = \frac{1}{2}k_s x^2 + \frac{1}{2}k_s y^2 + \frac{1}{2}k_s z^2 \quad (2.11)$$

where  $k_s$  is the spring constant.

From quantum mechanics, we know that a harmonic oscillator can store energy

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega_0 \quad n = 0, 1, 2, \dots \quad (2.12)$$

where  $\hbar = \frac{h}{2\pi}$  is the reduced Planck's constant and  $\omega_0 = \sqrt{k_s/m}$  is the natural frequency of the oscillator.

Beyond the zero-point energy of  $\hbar\omega_0/2$  per oscillator, each oscillator can store any non-negative integer number of “quanta” of energy. A microstate of this system is defined by the number of quanta stored in each oscillator. A macrostate is defined by the *total* number of quanta (a non-negative integer which we call  $q$ ) stored in all the oscillators combined.

To see how to count states and construct the multiplicity  $\Omega(N, q)$ , consider the case  $N = 2$ :

#1	#2		
0	0	$q = 0$	$\Omega(2, 0) = 1$
1	0	$q = 1$	$\Omega(2, 1) = 2$
0	1		
2	0	$q = 2$	$\Omega(2, 2) = 3$
1	1		
0	2		

continuing, we would find  $\Omega(2, 3) = 4$ , etc., which can be summarized as  $\Omega(2, q) = q + 1$ . We can also note that the  $N = 1$  case is quite simple, since there's only one place to put all the quanta of energy, so  $\Omega(1, q) = 1$ .

The combinatorics for the general case are equivalent to the problem of how to arrange  $q$  marbles in  $N$  bins. One could attack this head-on by dropping the marbles one at a time and asking how many places there are to put each of them, but a little bit of fancy footwork would be necessary to get it right. (In particular, to account for the different arrangements of the  $q$  marbles.) It turns out to be clearer to focus on the “dividers” between the bins. If there are  $N$  bins, there are  $N - 1$  dividers between them. Placing the  $q$  marbles into the  $N$  bins is equivalent to lining up the marbles and then laying down the dividers between them. We'll initially treat the  $N - 1$  dividers as different and then divide by  $N - 1$  to account for rearrangements of the dividers.

When we lay down the first divider, there are  $q + 1$  places to put it, since it could be in between any of the marbles, or at either end of the line. When we lay down the second

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<sup>1</sup>This leaves us in the unfortunate notational situation that  $N$  does *not* refer to the number of atoms or molecules in the system, which it usually does.

divider, there are  $q$  marbles plus a divider, so  $q + 1$  objects and thus  $q + 2$  different places to put the divider. When we lay down the third divider, there are  $q + 2$  objects already in the arrangement, so  $q + 3$  places to put it. This continues for all  $N - 1$  dividers, so the number of ways to lay down all of them is

$$\underbrace{(q + 1) \cdot (q + 2) \cdot \dots \cdot (q + N - 1)}_{N - 1 \text{ factors}} = \frac{(q + N - 1)!}{q!} \quad (2.13)$$

However, we have counted as different each rearrangement of the dividers, so we have to divide by  $N - 1$  to account for that. This makes the multiplicity

$$\Omega(N, q) = \frac{(q + N - 1)!}{q!(N - 1)!} = \binom{q + N - 1}{q} \quad (2.14)$$

Schroeder derives this in a slightly cuter way by pointing out that the multiplicity is the number of ways of choosing  $q$  marbles and  $N - 1$  dividers out of  $q + N - 1$  objects.

### 3 Interacting Systems

*In conjunction with this topic, you should read Section 2.3 of Schroeder.*

We've talked about the idea that if every microstate is equally likely, the probability of being in a given macrostate is its multiplicity divided by the total number of microstates. We also have a formula (2.14) for the multiplicity of a macrostate in a given toy model, namely the Einstein solid. But we can't just look at a single Einstein solid and talk about the probability of it having a given number of quanta of energy stored in it. For one thing, the number of *all* microstates is infinite. Also, more importantly, conservation of energy prevents an isolated solid from moving from one macrostate to another.

What we can do is consider two Einstein solids in contact with each other. The system is described by the number of oscillators:  $N_A$  in the first solid and  $N_B$  in the second solid. A macrostate of the system is then labelled by the number of quanta of energy in each solid:  $q_A$  in the first solid and  $q_B$  in the second solid. For each of the  $\Omega_A = \Omega(N_A, q_A)$  ways to arrange the  $q_A$  quanta of energy in the first solid, any of the  $\Omega_B = \Omega(N_B, q_B)$  ways of arranging the  $q_B$  quanta in the second solid is possible. So the overall multiplicity, the total number of microstates which have  $q_A$  energy units in the first solid and  $q_B$  in the second, is

$$\Omega_{\text{tot}} = \Omega(q_A, q_B) = \Omega_A(q_A)\Omega_B(q_B) \quad (3.1)$$

If the two solids can only interact with each other, and are isolated from the rest of the universe, the *total* amount of energy will remain constant:

$$q_A + q_B = q_{\text{tot}} = \text{constant} \quad (3.2)$$

Then we can say what the probability is that there will be exactly  $q_A$  quanta of energy in the first solid (in which case there must be  $q_{\text{tot}} - q_A$  in the second):

$$P(q_A) = \frac{\Omega_A(q_A)\Omega_B(q_{\text{tot}} - q_A)}{\sum_{q'_A} \Omega_A(q'_A)\Omega_B(q_{\text{tot}} - q'_A)} \quad (3.3)$$

The denominator is just the total number of microstates with a total of  $q_{\text{tot}}$  quanta of total energy stored in the solids. Note that this is the same as the multiplicity of the state of an Einstein solid with  $q_{\text{tot}}$  quanta of energy stored in  $N_A + N_B$  oscillators, i.e.,

$$\binom{q_{\text{tot}} + N_A + N_B - 1}{q_{\text{tot}}} \quad (3.4)$$

For a small-scale problem, say two Einstein solids with 3 oscillators each ( $N_A = 3 = N_B$ ), sharing 4 quanta of energy between them ( $q_{\text{tot}} = 4$ ), we can work out the multiplicities of the various macrostates by hand:

$q_A$	$\Omega_A$	$q_B$	$\Omega_B$	$\Omega_{\text{tot}} = \Omega_A \Omega_B$	$P(q_A) = \frac{\Omega_{\text{tot}}}{126}$
0	1	4	15	15	11.9%
1	3	3	10	30	23.8%
2	6	2	6	26	28.6%
3	10	1	3	30	23.8%
4	15	0	1	15	11.9%

We see that for these two identical solids, the most likely arrangement of energy is half in one, half in the other. If we up the size of the system to  $N_A = 50 = N_B$  and  $q_{\text{tot}} = 20$ , we can still handle it with the aid of a spreadsheet program. (See Figure 1.) Note that for this larger system, the most likely macrostate is still with half the energy in each solid, but now the probability distribution, when viewed on the scale of the range of possible  $q_A$  values, is sharper. While the probability of the most likely macrostate has gone down from 29% to 16%, the probability that  $q_A$  is between  $\frac{3}{8}$  and  $\frac{5}{8}$  of  $q_{\text{tot}}$  has gone up from 29% to 69%. (That’s the significance of the “coarse prob” column, which adds up the probabilities of the macrostates of the larger system which come closest to each macrostate of the smaller system.)

Schroeder gives an example of an even larger system, with  $N_A = 300$ ,  $N_B = 200$ , and  $q_{\text{tot}} = 100$ , where the probability is even more sharply peaked about the most likely macrostate.

So if the two solids start out with a distribution of energy away from the peak of  $\Omega_{\text{tot}}$ , and we let them exchange energy for a while, so that each allowed microstate is equally likely, they’re statistically very likely to end up in a macrostate near the peak of the probability distribution. This is a manifestation of the **Second Law of Thermodynamics**, seen as a probabilistic statement: It’s very unlikely that a system will end up in a state much different from the state of maximum multiplicity.

For a real macroscopic system, the probability distribution is *very* sharp indeed, since  $N_A$ ,  $N_B$ , and  $q_{\text{tot}}$  are all around  $10^{23}$ . But before we can make a quantitative statement about this, we have to attack a mathematical challenge. The multiplicity expressions involve factorials, and how in the world would we take the factorial of a number as large as  $10^{23}$ , which is defined as the product of the first  $10^{23}$  positive integers. Even if you could multiply a billion numbers per second, it would still take  $10^{14}$  seconds  $\approx$  3 million years. And the answer would be far too long to write on all the paper in the world.

Sheet1

qA	OmegaA	qB	OmegaB	Omegatot	Prob	Coarse Prob	4*qA/qtot
0	1	20	1.156E+17	1.1563E+17	0.0005%	0.0559%	0
1	50	19	3.352E+16	1.6758E+18	0.0068%		0.2
2	1275	18	9.365E+15	1.194E+19	0.0486%		0.4
3	22100	17	2.516E+15	5.5602E+19	0.2265%		0.6
4	292825	16	6.480E+14	1.8976E+20	0.7729%		0.8
5	3162510	15	1.595E+14	5.0448E+20	2.0548%	15.3167%	1
6	28989675	14	3.739E+13	1.0838E+21	4.4145%		1.2
7	231917400	13	8.308E+12	1.9268E+21	7.8480%		1.4
8	1.652E+09	12	1.742E+12	2.8786E+21	11.7246%		1.6
9	1.065E+10	11	3.427E+11	3.6494E+21	14.8639%		1.8
10	6.283E+10	10	6.283E+10	3.9474E+21	16.0778%	69.2548%	2
11	3.427E+11	9	1.065E+10	3.6494E+21	14.8639%		2.2
12	1.742E+12	8	1.652E+09	2.8786E+21	11.7246%		2.4
13	8.308E+12	7	231917400	1.9268E+21	7.8480%		2.6
14	3.739E+13	6	28989675	1.0838E+21	4.4145%		2.8
15	1.595E+14	5	3162510	5.0448E+20	2.0548%	15.3167%	3
16	6.480E+14	4	292825	1.8976E+20	0.7729%		3.2
17	2.516E+15	3	22100	5.5602E+19	0.2265%		3.4
18	9.365E+15	2	1275	1.194E+19	0.0486%		3.6
19	3.352E+16	1	50	1.6758E+18	0.0068%		3.8
20	1.156E+17	0	1	1.1563E+17	0.0005%	0.0559%	4
<b>2.4552E+22</b>					100.000%		

NA= 50

NB= 50

qtot= 20

Figure 1: Multiplicities and probabilities for two Einstein solids. Table generated by a numeric spreadsheet. (Excel version)



## 4 Large Numbers

*In conjunction with this topic, you should read Section 2.4 of Schroeder.*

The first thing to note is that when defining a number as “large”, we need to be talking about a dimensionless quantity. Otherwise there’s no absolute statement that something is large or small; for example, an energy of 1 J doesn’t sound large, but if we write it as  $6.24 \times 10^{18}$  eV it’s a different story.

Now, note that we can deal exactly with integers like  $2! = 2$ ,  $4! = 24$ ,  $6! = 720$ , and even  $8! = 40,320$ . But at some point it becomes impractical, to write  $14! = 87,178,291,200$  or  $18! = 6,402,373,705,728,000$ . But as Physicists, we have a natural solution to this problem. None of our physical quantities are measured exactly, and often we only know (or care about) three or four *significant figures*. So we’ll say

$$g = 9.807 \text{ m/s}^2 \tag{4.1}$$

which really means

$$9.8065 \text{ m/s}^2 \lesssim g \lesssim 9.8075 \text{ m/s}^2 \tag{4.2}$$

So we really couldn’t care less whether  $9! = 362,880$  or  $9! = 362,879$  because the fractional difference is less than the precision of our equations.

If we have a big integer but really don’t care what the last few digits are, we just use scientific notation and drop the last few digits, so

$$9! = 3.629 \times 10^5 \tag{4.3}$$

which means for all we care

$$362,850 = 3.6285 \times 10^5 \lesssim 9! \lesssim 3.6295 \times 10^5 = 362,950 \tag{4.4}$$

This makes it a lot more manageable to write

$$18! = 6.40 \times 10^{15}. \tag{4.5}$$

And this is our rough definition of what Schroeder means by a “large number”: a dimensionless numbers you wouldn’t want to write without scientific notation. The number of particles in a macroscopic object will always be a “large number”.

Implicit in this is that you’ll want to round off your large number, and not keep all the decimal places down to hundreds, tens and ones. So if you add a “small number” like 6 or 25 or 137, it won’t change the value to within the precision you care about, so e.g.,

$$6.40 \times 10^{15} + 137 = 6.40 \times 10^{15} \tag{4.6}$$

After all, we haven’t specified whether we mean

$$6,401,000,000,000,000$$

or

$$6,399,000,000,000,000$$

so adding 137 to this large number is completely “under the radar”.

## 4.1 Very Large Numbers

Now, in statistical physics, we find ourselves writing  $N!$  or  $e^N$  or  $N^N$  or  $10^N$  where  $N$  is a “large number”. The result is a “very large number”, which we can’t even comfortably write in scientific notation, e.g., if  $N = 6.022 \times 10^{23}$ ,

$$10^N = 10^{602,200,000,000,000,000,000,000} \quad (4.7)$$

but all the zeros in the exponent aren’t really zeros, so even that’s not right. For very large numbers, you’d need to write the exponent itself in scientific notation. Or take the logarithm and then write that in scientific notation.

This, then, is our definition of what Schroeder calls a “very large number”: a number whose logarithm is a “large number”, i.e., the logarithm needs to be written in scientific notation. And as a practical matter, we’ll ultimately want to deal with such numbers through their logarithms.

## 4.2 Stirling’s Approximation

As noted above, and recalling for example the multiplicity of an Einstein solid

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!(N - 1)!} \quad (4.8)$$

multiplicities tend to involve factorials of large numbers (in this case  $q$  and  $N$ ) which for a macroscopic system tend to be of order  $10^{23}$ . So  $q!$  and  $N!$  and  $(N - 1)!$  are very large numbers, whose logarithms we want write in scientific notation. So we need a method to approximate the logarithm of a very large number. (Note that if  $N$  is large, then  $N!$  is very large, but  $\ln N!$  is only large.)

Starting from the definition of the factorial

$$N! = 1 \cdot 2 \cdot 3 \cdot \dots \cdot (N - 1) \cdot N = \prod_{k=1}^N k \quad (4.9)$$

now, since

$$\ln(ab) = \ln a + \ln b, \quad (4.10)$$

we see

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + \dots + \ln(N - 1) + \ln N = \sum_{n=1}^N \ln n \quad (4.11)$$

Now for large  $N$ , we’ve broken the range from 1 to  $N$  into a large number of intervals, each of which is a small fraction of the full range. This makes the sum above a good approximation for a Riemann sum used in the definition of an integral:<sup>2</sup>

$$\begin{aligned} \ln N! &= \sum_{n=1}^N \ln n = \sum_{n=1}^N (\ln n)(\Delta n) \approx \int_1^N \ln n \, dn = [n \ln n - n]_1^N = N \ln N - N - (\ln 1 - 1) \\ &= N \ln N - N + 1 \approx N \ln N - N \end{aligned} \quad (4.12)$$

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<sup>2</sup>The indefinite integral  $\int \ln x \, dx = x \ln x - x$  is left as an exercise; it can be done by integration by parts, with  $u = \ln x$  and  $dv = dx$ . Also worthwhile (and easier) is to check that  $\frac{d}{dx}(x \ln x - x) = \ln x$ .

This is known as *Stirling's Approximation*:

$$\ln N! \approx N \ln N - N \quad (4.13)$$

Very rarely, we will need a better approximation (see the appendix of Schroeder for a definition)

$$N! \approx N^N e^{-N} \sqrt{2\pi N} \quad (4.14)$$

Taking the logarithm of (4.14) shows it differs from (4.13) by the addition of a term  $\frac{1}{2} \ln(2\pi N) \ll N$ .

### 4.3 Multiplicity for a Large System

Now we are finally ready to estimate the multiplicity of an Einstein solid when the number of oscillators  $N$  and the number of quanta of energy  $q$  are both large. In that case,

$$\Omega(N, q) = \frac{(q + N - 1)!}{q!(N - 1)!} \quad (4.15)$$

is a “very large number”, and we’ll want to deal with its logarithm (which is a “large number”). This is (applying Stirling’s approximation in the form (4.13))

$$\begin{aligned} \ln \Omega &= \ln(q + N - 1)! - \ln q! - \ln(N - 1)! \\ &\approx (q + N - 1) \ln(q + N - 1) - (q + N - 1) - q \ln q + q - (N - 1) \ln(N - 1) + (N - 1) \end{aligned} \quad (4.16)$$

Note that in general, when  $n$  and  $k$  and  $n - k$  are large, Stirling’s approximation tells us

$$\binom{n}{k} \approx n \ln n - k \ln k - (n - k) \ln(n - k) . \quad (4.17)$$

Also note that replacing  $N - 1$  with  $N$  makes a negligible change to  $\ln \Omega$ , so

$$\ln \Omega \approx (q + N) \ln(q + N) - q \ln q - N \ln N \quad (4.18)$$

Now, (4.18) is true in general for large  $q$  and  $N$ . We can obtain a slightly more enlightening approximation by specializing to the case where  $q \gg N$ , which is known as the “high energy limit”. In that case  $N/q$  is a small parameter and we write

$$\ln(q + N) = \ln \left( q \left[ 1 + \frac{N}{q} \right] \right) = \ln q + \ln \left( 1 + \frac{N}{q} \right) \quad (4.19)$$

Now for  $x \ll 1$ , we can use a Taylor series (see homework) to approximate

$$\ln(1 + x) \approx x \quad (4.20)$$

so that

$$\ln(q + N) \approx \ln q + \frac{N}{q} \quad (4.21)$$

and

$$\ln \Omega \approx \cancel{q \ln q} + q \frac{N}{q} + N \ln q + N \frac{N}{q} - \cancel{q \ln q} - N \ln N = N + \frac{N^2}{q} + N \ln q - N \ln N \approx N + N \ln \left( \frac{q}{N} \right) \quad (4.22)$$

where we have neglected  $\frac{N^2}{q} \ll N$ . (Note that we could not just neglect  $N$  compared to  $q$  off the bat, because the  $q \ln q$  terms cancelled, and we would have ended up neglecting  $N \ln q$ , which is as large as any of the terms which survive.)

Now, if we want to talk about the multiplicity (which is proportional to the probability of being in a particular macrostate), we have

$$\Omega \sim e^{N + N \ln \left( \frac{q}{N} \right)} = e^N \left( e^{\ln \left( \frac{q}{N} \right)} \right)^N = \left( \frac{eq}{N} \right)^N \quad (4.23)$$

which is indeed a very large number. In fact, to be careful we should state this as

$$\ln \Omega \approx \ln \left[ \left( \frac{eq}{N} \right)^N \right] ; \quad (4.24)$$

The “ $\sim$ ” appearing in (4.23) means that it is only correct give or take “large” (but not “very large”) factors.

#### 4.3.1 Probabilities for Interacting Large Einstein Solids

## 5 The Ideal Gas

*In conjunction with this topic, you should read Section 2.5 of Schroeder.*

## 6 Entropy

*In conjunction with this topic, you should read Section 2.6 of Schroeder.*

## A Appendix: Correspondence to Class Lectures

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2004 January 27	1–2	2–6
2004 January 29	3–4.1	6–10
2004 February 3	4.2–4.3	10–12
2004 February 5	5	12–12
2004 February 10	6	12–12