Physics 352 Foundations of Physics II Davison E. Soper

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### 1 Temperature

Temperature is a measure of the tendency of a body to spontaneously transfer energy to its surroundings. For instance if you put a body with a higher temperature in "thermal contact" with a body with a lower temperature, the hot body will transfer energy to the cold body. The temperature of the hot body will decrease and the temperature of the cold body will increase. This process slows down as the temperatures of the two bodies become the same.

For a quantitative measure of temperature, we can use an ideal gas, which is a pretty good approximation for a real gas as long as the number of molecules per unit volume in the gas is small enough so that there is lots of space between the molecules and as long as the gas is hot enough so that classical mechanics rather than quantum mechanics applies. For N molecules of an ideal gas with pressure P, V and temperature T we have

$$PV = NkT.$$
 (1)

Here k is the Boltzmann constant, which effectively converts energy units into temperature units. Its value is  $k = 1.4 \times 10^{-23}$  J/K. Here K is the abbreviation for *kelvins*, the standard SI unit for temperature. On the kelvin scale, water freezes at 273 K and boils at 373 K.

What is the status of this? First of all, it says that at constant temperature, P is proportional to 1/V. We don't need to have a temperature scale defined to establish this by experiment. Second, since we have not yet defined a temperature scale, we can use this as the definition of T. One can call this the "ideal gas temperature scale." Later, we will see that there is a more general definition that gives the same result. For now, we go on in the next section to find that there is an interesting relation between T, thus defined, and how fast the molecules in a gas are moving.

## 2 Microscopic model for an ideal gas

Let's suppose that we have N molecules of gas in a box of volume V. Let each molecule have mass m. The atoms don't exert any forces on each other except when they are very close together, and the average separation between molecules is much bigger than the distance at which the molecules exert forces on each other.

We consider a small piece of container wall of area  $\Delta A$  oriented perpendicular to the *x* axis, with the gas in the region x < 0. We will keep the model simple by supposing that the walls of the container are perfectly smooth on a microscopic scale. Then, when a molecule with momentum  $m\vec{v}$  hits the wall, it bounces off with momentum  $m\vec{v}'$ , with  $mv'_y = mv_y$  and  $mv'_z = mv_z$  but  $mv'_x = -mv_x$ . Thus it transfers a tiny bit of momentum  $2mv_x \hat{x}$  to the wall.

Now let's suppose that we have N/2 molecules with the same velocity  $\vec{v}$ and N/2 molecules with the same  $v_y$  and  $v_z$  but with  $v_x$  reversed. (These are the ones that have bounced off the wall and are heading away.) Let these molecules uniformly fill the container. Then the number of molecules that hit our little area of wall in time  $\Delta t$  is  $v_x \Delta t \Delta A (N/2)/V$ . The total momentum that they deliver is this number of molecules times the momentum delivered by each:

$$2m v_x^2 \Delta t \Delta A (N/2)/V.$$
<sup>(2)</sup>

Since momentum transfer per unit time is force, the force on the wall is

$$m v_x^2 \Delta A N/V.$$
 (3)

Since force per unit area is pressure, the pressure on the wall is

$$m v_x^2 N/V. (4)$$

Now it wasn't very realistic to suppose that we have only molecules with a fixed velocity  $\vec{v}$ , so lets suppose that we have  $N_1$  molecules with velocity  $\vec{v}_1$ ,  $N_2$  molecules with velocity  $\vec{v}_2$ , and in general  $N_j$  momentum  $\vec{v}_j$ . Each kind of molecule exerts its own pressure, so that the total pressure is

$$P = \sum_{j} m v_{j,x}^2 N_j / V.$$
(5)

The total number of molecules is  $N = \sum N_j$ . Thus

$$PV = N \ \frac{\sum_j N_j m v_{j,x}^2}{\sum_j N_j}.$$
(6)

Now in general if we have  $N_j$  things of kind j and each thing has some quantity  $Q_j$  then we define the average Q of the things as

$$\langle Q \rangle = \frac{\sum_j N_j Q_j}{\sum_j N_j}.$$
(7)

With this notation,

$$PV = N \langle mv_x^2 \rangle. \tag{8}$$

We now assume that our gas is isotropic, so that

$$\langle mv_x^2 \rangle = \langle mv_y^2 \rangle = \langle mv_z^2 \rangle. \tag{9}$$

Then

$$\langle mv_x^2 \rangle = \frac{1}{3} \left( \langle mv_x^2 \rangle + \langle mv_y^2 \rangle + \langle mv_z^2 \rangle \right). \tag{10}$$

or

$$\langle m v_x^2 \rangle = \frac{1}{3} \langle m \vec{v}^2 \rangle. \tag{11}$$

Thus

$$PV = \frac{1}{3} N \langle m\vec{v}^2 \rangle.$$
(12)

We recognize that  $\frac{1}{2}m\vec{v}^2$  is kinetic energy, so we write this result as

$$PV = \frac{2}{3} N \left\langle \frac{1}{2} m \vec{v}^2 \right\rangle. \tag{13}$$

Now recall that experiment gives the ideal gas law

$$PV = NkT \tag{14}$$

if we adopt the ideal gas definition of T. Thus we find out what T is:

$$\frac{3}{2}kT = \langle \frac{1}{2}m\vec{v}^2 \rangle. \tag{15}$$

Notice that this says that the velocity of the molecules would go to zero if we lowered the temperature to zero. But that isn't right. We used classical mechanics to make the model, but it would become necessary to use quantum mechanics. Since we know about quantum mechanics, we can see what the problem is. Let's suppose that each molecule has to live in a little box of length L such that  $NL^3 = V$ . That is,  $L = [V/N]^{1/3}$ . Then the lowest energy

the molecule in this box could have is  $\hbar^2 \pi^2 / (2mL^2)$ . We will certainly need to use quantum mechanics instead of classical mechanics if the average kinetic energy is comparable to this minimum energy. Thus our classical model applies if

$$\frac{3}{2}kT \gg \frac{\hbar^2 \pi^2}{2mL^2}.$$
 (16)

Inserting our formula for L, the requirement is

$$kT \gg \frac{\hbar^2 \pi^2}{3 m} \left(\frac{N}{V}\right)^{2/3}.$$
 (17)

We can see what this means numerically by writing is as

$$kT \gg \frac{\hbar^2 \pi^2}{3m} \left(\frac{P}{kT}\right)^{2/3}.$$
 (18)

This is equivalent to

$$(kT)^3 \gg \left(\frac{\hbar^2 \pi^2}{3 m}\right)^3 \left(\frac{P}{kT}\right)^2.$$
<sup>(19)</sup>

or

$$(kT)^5 \gg \left(\frac{\hbar^2 \pi^2}{3\,m}\right)^3 P^2,$$
 (20)

or, finally,

$$T \gg \frac{1}{k} \left(\frac{\hbar^2 \pi^2}{3 \, m}\right)^{3/5} P^{2/5},$$
 (21)

Let's put  $P = 1 \times 10^5$  N/m<sup>2</sup>, which is approximately normal air pressure, into this along with  $m = 28 \times 1.67 \times 10^{-27}$  kg (the mass of an N<sub>2</sub> molecule),  $\hbar = 1.055 \times 10^{-34}$  J s and  $k = 1.381 \times 10^{-23}$  J/K. You have enough problems to do, so I tried this. I got 0.4 K for the temperature at which things must go wrong.

There is another limitation on T at a given pressure in order for the ieal gas law to apply. Let d be the size of a molecule. Then the distance L between molecules has to be much bigger than d. That is, we need

$$\frac{V}{N} \gg d^3. \tag{22}$$

Using

$$\frac{V}{N} = \frac{kT}{P},\tag{23}$$

the required condition is

$$T \gg \frac{P}{k} d^3. \tag{24}$$

If we use our previous numbers together with the (rough) estimate  $d = 2 \times 10^{-10}$  m, one obtains 0.06 K for this temperature at which the ideal gas law must go wrong.

At normal air pressure, nitrogen turns to a liquid at about 77 K, so the  $\gg$  sign in the arguments above really means that T has to be much bigger the ciritical values that we calculated.

# 3 Getting to equilibrium

Imagine a system made of N harmonic oscillators, each with natural angular frequency  $\omega_0$ . We have studied oscillators in classical mechanics, but here we want to use quantum mechanics. In quantum theory, the energy of a harmonic oscillator is quantized. The only allowed values are

$$E_j = (j + \frac{1}{2})\hbar\omega_0 \tag{25}$$

where j can be 0, 1, 2 .... We have lots of oscillators. Let the state of the nth oscillator be labelled by  $j_n$ , so that the total energy of the system is

$$E = \sum_{n=1}^{N} (j_n + \frac{1}{2}) \hbar \omega_0 = \hbar \omega_0 \sum_{n=1}^{N} j_n + \frac{1}{2} N \hbar \omega_0.$$
 (26)

We can write this as

$$E = q\hbar\omega_0 + \frac{1}{2}N\hbar\omega_0 \tag{27}$$

where

$$q = \sum_{n=1}^{N} j_n. \tag{28}$$

Now we can ask, how many are the ways for our N oscillators to have J energy units above the ground state, as given in Eq. (??). In purely mathematical terms, how many ways are there to choose N non-negative integers  $j_n$  such that they sum to q? The result, elegantly proved in Schroeder, is

$$\Omega(N,q) = \frac{(q+N-1)!}{q!(N-1)!}.$$
(29)

Now suppose that we have two collections of oscillators, one with  $N_A$  oscillators and one with  $N_B$  oscillators. The first set of oscillators has  $q_A$  energy units above the ground state, while the second has  $q_B$  energy units. We imagine that the two collections are weakly coupled, so that  $q_A$  and  $q_B$  can change as long as  $q_A + q_B$  remains the same. Let us denote

$$\frac{q_A + q_B}{N_A + N_B} = r. \tag{30}$$

Let's suppose that we measure  $q_A$  and  $q_B$  to see what happens. We will call the state specified by  $\{q_A, q_B\}$  a *macrostate*. We call the exact state of all the oscillators a *microstate*. Then there are lots of microstates for each macrostate.

We assume that in an isolated system in thermal equilibrium, all accessible microstates are equally probable. In this situation, this assumption amounts to saying that all the microstates corresponding to a given macrostate  $\{q_A, q_B\}$  are equally likely.

As noted above there are lots of microstates for each macrostate. In fact, the number is

$$\Omega(N_A, q_A)\Omega(N_B, q_B). \tag{31}$$

To formulate this a little more precisely, let

$$q_A = rN_A + \delta q$$
  

$$q_B = rN_B - \delta q.$$
(32)

This builds in the constraint that  $q_A + q_B$  is fixed by Eq. (??). Then the macrostate is labelled by  $\delta q$ . The total number of microstates corresponding to macrostate  $\delta q$  is

$$\Omega(\delta q) = \Omega(N_A, rN_A + \delta q) \,\Omega(N_B, rN_B - \delta q). \tag{33}$$

The probability that the system is in macrostate  $\delta q$  is just this number  $\Omega(\delta q)$  divided by the total number of available microstates,

$$\Omega(\delta q) / (\sum_{\delta q'} \Omega(\delta q')).$$
(34)

Let's now see what  $\delta q$  is most likely. We look for the value of  $\delta q$  that makes  $\log \Omega(\delta q)$  biggest. We assume that  $N_A$  and  $N_B$  are very large and use the approximation

$$\log n! = n \log n - n + \frac{1}{2} \log(2\pi n) + \mathcal{O}(1/n).$$
(35)

Here  $\mathcal{O}(1/n)$  indicates terms that go to zero at least as fast as 1/n as  $n \to \infty$ . This is called *Stirling's approximation*.

Using this approximation, we have

$$\log \Omega(N_A, rN_A + \delta q) = (N_A[1+r] + \delta q - 1) \log(N_A[1+r] + \delta q - 1) -(N_A[1+r] + \delta q - 1) + \frac{1}{2} \log(2\pi [N_A[1+r] + \delta q - 1]) -[N_Ar + \delta q] \log(N_Ar + \delta q) +[N_Ar + \delta q] - \frac{1}{2} \log(2\pi [N_Ar + \delta q]) -(N_A - 1) \log(N_A - 1) +(N_A - 1) - \frac{1}{2} \log(2\pi [N_A - 1]) +\mathcal{O}(1/N_A).$$
(36)

When we write  $\mathcal{O}(1/N_A)$  here, we mean things that go to zero as  $N_A \to \infty$  with r fixed and  $\delta q/N_A$  fixed (but possibly  $\delta q/N_A$  small or zero). Some of the terms cancel, leaving

$$\log \Omega(N_A, rN_A + \delta q) = (N_A[1+r] + \delta q - 1) \log(N_A[1+r] + \delta q - 1) + \frac{1}{2} \log(2\pi [N_A[1+r] + \delta q - 1]) - [N_A r + \delta q] \log(N_A r + \delta q) - \frac{1}{2} \log(2\pi [N_A r + \delta q]) - (N_A - 1) \log(N_A - 1) - \frac{1}{2} \log(2\pi [N_A - 1]) + \mathcal{O}(1/N_A).$$
(37)

To find out where  $\log \Omega(N_A, rN_A + \delta q) + \log \Omega(N_B, rN_B - \delta q)$  is maximum, we want to differentiate with respect to  $\delta q$ . We get

$$\frac{\partial \log \Omega(N_A, rN_A + \delta q)}{\partial \delta q} = \log(N_A[1+r] + \delta q - 1) + 1$$

$$+ \frac{1}{2} \frac{1}{N_A[1+r] + \delta q - 1}$$

$$- \log(N_A r + \delta q) - 1$$

$$- \frac{1}{2} \frac{1}{N_A r + \delta q}$$

$$+ \mathcal{O}(1/N_A). \qquad (38)$$

Two of the terms here are of order  $1/N_A$ , so we drop them. There is a +1 that cancels against a -1. Finally,  $\log(N_A[1+r] + \delta q - 1)$  is  $\log(N_A[1+r] + \delta q) + \mathcal{O}(1/N_A)$ , so we can throw away the +1 inside the logarithm. Thus

$$\frac{\partial \log \Omega(N_A, rN_A + \delta q)}{\partial \delta q} = \log(N_A[1+r] + \delta q) - \log(N_A r + \delta q) + \mathcal{O}(1/N_A), \quad (39)$$

or

$$\frac{\partial \log \Omega(N_A, rN_A + \delta q)}{\partial \delta q} = \log \left( \frac{[1+r] + \delta q/N_A}{r + \delta q/N_A} \right) + \mathcal{O}(1/N_A).$$
(40)

This has simplified a lot! For the B oscillators we have

$$\frac{\partial \log \Omega(N_B, rN_B - \delta q)}{\partial \delta q} = -\log \left(\frac{[1+r] - \delta q/N_B}{r - \delta q/N_B}\right) + \mathcal{O}(1/N_B).$$
(41)

Thus

$$\frac{\partial \log \Omega(\delta q)}{\partial \delta q} = \log \left( \frac{[1+r] + \delta q/N_A}{r + \delta q/N_A} \right) - \log \left( \frac{[1+r] - \delta q/N_B}{r - \delta q/N_B} \right) + \mathcal{O}(1/N_A, 1/N_B).$$
(42)

Where is  $\log \Omega(\delta q)$  maximum? Evidently it is where  $\delta q = 0$ . (We will check that it is a maximum and not a minimum below.) That is, the maximum is at  $q_A = rN_A$  and  $q_B = rN_B$ . Thus the most likely situation is that the oscillators in group A have the same amount of energy per oscillator as the oscillators in group B. If, say, the oscillators of group A have more energy per oscillator than the oscillators of group B before we put the two groups together, it is not likely that they will stay that way. The most likely thing is that the oscillators of group A will lose energy and those of group B will gain energy until the energy per oscillator in each group is the same. We say that group A cools down, while group B heats up.

Now lets look at  $\log \Omega(\delta q)$  in more detail. For small  $\delta q$  (small compared to  $N_A$  or  $N_B$ ) we can write

$$\log \Omega(\delta q) \approx \log \Omega(0) - \frac{1}{2} C(\delta q)^2$$
(43)

where

$$C = -\left[\frac{\partial^2 \log \Omega(\delta q)}{\partial \delta q^2}\right]_{\delta q=0}.$$
(44)

We can compute C:

$$C = -\frac{1}{N_A} \left[ \frac{1}{1+r} - \frac{1}{r} \right] - \frac{1}{N_B} \left[ \frac{1}{1+r} - \frac{1}{r} \right] = \frac{N_A + N_B}{N_A N_B} \frac{1}{r(1+r)}.$$
(45)

First of all, we verify that C > 0, so that  $\log(\Omega)$  has a maximum and not a minimum at  $\delta q = 0$ . Second, we get an approximation for  $\Omega(\delta q)$  that is quite instructive

$$\Omega(\delta q) \approx \Omega(0) \, \exp(-\frac{1}{2} C(\delta q)^2). \tag{46}$$

Macrostates with  $\delta q$  much larger than  $1/\sqrt{C}$  are quite unlikely. What our calculation shows is that C is proportional to  $N = N_A + N_B$  (assuming that  $N_A/N_B$  is of order 1, not very big or very small.) Thus the typical fluctuations in  $\delta q$  are of order  $\sqrt{N}$  and the typical fluctuations in the energy per oscillator,  $\delta q/N$ , are of order  $1/\sqrt{N}$ . Now if N is something like  $10^{23}$ , then  $\sqrt{N}$  is still a very big number. Thus there are fluctuations in the energy per oscillator – sometimes the oscillators of group A have a little more energy, sometime the oscillators of group B have a little more energy. However the fluctuations in the energy per oscillator are very small for a big system.

### 4 Counting states for the ideal gas

We have seen how to count the multiplicity of states having a given energy in the case of a collection of two state spins in a magnetic field and for a collection of independent harmonic oscillators. Here we try the ideal gas.

Suppose that we have N structureless gas molecules in a cubic box of length L, volume  $V = L^3$ . What are the possible states? Recall the particle in a one dimensional box. The particle can have a wave function proportional to  $\sin(\pi nx/L)$ , so that the wave function vanishes at x = 0 and at x =L. Here n can be any positive integer. The particle has momentum p = $\hbar \pi n/L = n h/(2L)$ , or more properly, it has momentum either plus or minus this amount, since the standing wave is a linear combination of a left-moving and a right-moving wave. The molecule's energy is

$$E = \frac{p^2}{2m}.$$
(47)

Now our molecules can move in a three dimensional box. The generalization of the states is simple:

$$E = \frac{p_1^2 + p_2^2 + p_3^2}{2m} \tag{48}$$

where

$$p_j = \frac{n_j h}{2L} \tag{49}$$

with positive integers  $\{n_1, n_2, n_3\}$ . Now, we have N molecules. Let the Jth molecule have momentum

$$p_{J,j} = \frac{n_{J,j}h}{2L}.$$
(50)

All of the  $n_{J,j}$  are positive integers. The total energy of the system is then

$$U = \frac{1}{2m} \sum_{J=1}^{N} \sum_{j=1}^{3} p_{J,j}^{2}.$$
 (51)

Lets try to answer the question, "How many states of the gas are there with energy between U and  $U + \delta U$ ?" The answer is evidently

$$\Omega = \sum_{n_{1,1}} \sum_{n_{1,2}} \sum_{n_{1,3}} \cdots \sum_{n_{N,3}} \theta \left( U < \frac{1}{2m} \sum_{J=1}^{N} \sum_{j=1}^{3} p_{J,j}^{2} < U + \delta U \right)$$
(52)

where  $\theta(\dots)$  is one when the condition indicated is true, zero when it is false. Of course, if N is large, this is an "in principle" formula but is not of much practical use. We can, however, approximate. Each sum is approximately an integral,

$$\sum_{n} \to \frac{2L}{h} \int_{0}^{\infty} dp = \frac{L}{h} \int_{-\infty}^{\infty} dp.$$
 (53)

The factor 2L is from the step size  $\Delta n = (2L/h)\Delta p$ . Thus

$$\Omega = \left(\frac{V}{h^3}\right)^N \int dp_{1,1} \int dp_{1,2} \int dp_{1,3} \cdots \int dp_{N,3} \,\theta\left(U < \frac{\vec{P}^2}{2m} < U + \delta U\right) \tag{54}$$

where

$$\vec{P}^2 \equiv \sum_{J=1}^{N} \sum_{j=1}^{3} p_{J,j}^2.$$
(55)

As the notation indicates, you are invited to think of  $\vec{P}$  as a vector in 3N dimensions with components  $p_{J,j}$  Here I have replaced  $L^3$  by V. This is the volume of a thin shell in  $\vec{P}$  space. The width of the shell is given by

$$\frac{2P\delta P}{2m} = \delta U \tag{56}$$

or

$$\delta P = \frac{m}{P} \,\delta U \tag{57}$$

where  $P = \sqrt{\vec{P^2}}$  and, on the shell,  $P = \sqrt{2mU}$ . With this notation,

$$\Omega = \left(\frac{V}{h^3}\right)^N \int dp_{1,1} \int dp_{1,2} \int dp_{1,3} \cdots \int dp_{N,3} \,\theta \left(\sqrt{2mU} < P < \sqrt{2mU} + \delta P\right)$$
(58)

The integral here is just  $\delta p$  times the surface area of a sphere in 3N dimensions,

$$\Omega = \left(\frac{V}{h^3}\right)^N \frac{m\,\delta U}{P} A(P,3N) \tag{59}$$

We certainly know that this area is proportional to  $P^{3N-1}$ ,

$$A(P,3N) = P^{3N-1}A(1,3N).$$
(60)

It is fairly easy to find the surface area of a unit sphere in 3N dimensions. I skip the derivation and just state the result,

$$A(1,3N) = \frac{2\pi^{3N/2}}{(3N/2 - 1)!}.$$
(61)

Thus

$$\Omega = \left(\frac{V}{h^3}\right)^N m \,\delta U \, P^{3N-2} \frac{2\pi^{3N/2}}{(3N/2 - 1)!} \tag{62}$$

Lets restate this in terms of U, using  $P = \sqrt{2mU}$ :

$$\Omega = \left(\frac{V}{h^3}\right)^N U^{3N/2} \frac{(2\pi m)^{3N/2}}{(3N/2 - 1)!} \frac{\delta U}{U}.$$
(63)

There is one more ingredient that we need. The new ingredient does not affect the dependence on V or U, but it does affect how U depends on N. We have assumed that if molecule 285 is on state  $\alpha$  and molecule 862 is in state

 $\beta$ , that's a different state from the state of the gas with molecule 285 in state  $\beta$  and molecule 862 in state  $\alpha$ . If the molecules are all the same, this doesn't seem right, and the rules of quantum mechanics say it isn't right. Instead, states that differ by interchanging identical particles are physically the *same* state. Thus we have overcounted, and we should divide by the number of ways, N, of interchanging the particles. Thus

$$\Omega = \left(\frac{V}{h^3}\right)^N U^{3N/2} \frac{(2\pi m)^{3N/2}}{N!(3N/2 - 1)!} \frac{\delta U}{U}.$$
(64)

Later on in the course, we will talk about what happens if we have two kinds of molecules, say  $O_2$  and  $N_2$ . Then the N! factors will make a difference.

Let's take the logarithm of this, using Stirling's approximation. We get

$$\frac{1}{N}\log\Omega \approx \log\left(\frac{V}{N}\left(\frac{U}{N}\right)^{3/2}\left(\frac{4\pi m}{3h^2}\right)^{3/2}\right) + \frac{5}{2},\tag{65}$$

where we have thrown away terms on the right hand side that vanish as  $N \to \infty$ . (There are terms in log  $\Omega$  that either grow like log N or are constant as  $N \to \infty$ . After we divide by N to make  $(1/N) \log \Omega$ , these terms divided by N vanish as  $N \to \infty$  so we have neglected them.)

#### 5 Entropy

We have seen that  $\Omega$  is important for statistical physics. For instance, suppose we have a system A with energy  $U_A$  and a system B with energy  $U_B$ , and we allow these systems to share energy. That is,  $U_A$  and  $U_B$  can change, keeping  $U_A + U_B = U_{\text{tot}}$  constant. The total multiplicity of states is  $\Omega_A \Omega_B = \Omega_{tot}$ . The most likely outcome is that  $U_A$  and  $U_B$  adjust themselves so that  $\Omega_{\text{tot}}$  is maximized.

The statistical meaning of  $\Omega$  is clear, but we have preferred to deal with  $\log \Omega$  in our calculations. There are three reasons for this. First,  $\log \Omega$  is not as huge as  $\Omega$ . Second, in simple cases, we can use approximations to help calculate  $\log \Omega$ . Third,  $\log \Omega_{\text{tot}} = \log \Omega_A + \log \Omega_B$ , so  $\log \Omega$  is "additive" like U.

We give a special name to  $\log \Omega$ , or rather to k times  $\log \Omega$ . We call this quantity the *entropy* S:

$$S = k \log \Omega. \tag{66}$$

For our two systems that can share energy, then, we want to find how to divide the total energy  $U_{\text{tot}}$  into energies  $U_A$  and  $U_B$  in such a way that the total entropy  $S_{\text{tot}} = S_A(U_A) + S_B(U_B)$  is maximized.

To make this more concrete, let's go back to our two Einstein solids. For an Einstein solid with N oscillators and energy U above the lowest energy state, we found

$$\Omega = \frac{[N + U/(\hbar\omega_0)]!}{[U/(\hbar\omega_0)]!N!}$$
(67)

where  $U/(\hbar\omega_0)$  is what we called q. Applying Stirling's approximation to this, we get

$$S(U) \approx Nk \left\{ \log \left( 1 + \frac{U}{N\hbar\omega_0} \right) - \frac{U}{N\hbar\omega_0} \log \left( \frac{\frac{U}{N\hbar\omega_0}}{1 + \frac{U}{N\hbar\omega_0}} \right) \right\}$$
(68)

where terms in S/N that vanish as  $N \to \infty$  are neglected. Then simple differentiation gives

$$\frac{dS(U)}{dU} = -\frac{k}{\hbar\omega_0} \log\left(\frac{\frac{U}{N\hbar\omega_0}}{1 + \frac{U}{N\hbar\omega_0}}\right).$$
(69)

If we have two systems that can share energy, then we want

$$\frac{dS_A(U_A)}{dU_A} + \frac{dS_B(U_{\rm tot} - U_A)}{dU_A} = 0.$$
 (70)

or

$$\frac{dS_A(U_A)}{dU_A} = \frac{dS_B(U_B)}{dU_B}.$$
(71)

The solution is

$$\frac{U_A}{N_A} = \frac{U_B}{N_B},\tag{72}$$

just as we found earlier.

Note that the particular result  $U_A/N_A = U_B/N_B$  is special for our very simple system of oscillators. But Eq. (??) is very general. We could apply it to two samples of the simple spin system that we studied. We could (and will) apply it to two containers of ideal gas. We could apply it to the Einstein solid oscillators interacting with an ideal gas, *et cetera*. We will look into all of this next quarter.

## 6 The Second Law of Thermodynamics

If you allow two systems to interact, the systems come to a macrostate that corresponds to the most possible microstates of the combined system. This maximizes the total entropy. That is,

#### Entropy gets bigger.

We will study the implications of this further next quarter. What we would like to do is go over to the ocean and get some water, turn it into hydrogen and oxygen using as an energy souce the thermal energy of the ocean – just cooling down the ocean. Then we can sell the hydrogen to the government to power cars. This will allow us to finance a class field trip to Tahiti in May. Unfortunately, the law stated above prevents us from profiting from this scheme.