PHY141 Lectures 20, 21 notes

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Contents

1 Introduction to thermal physics

1.1 Heat, Temperature and the Boltzmann constant

Up to this point we have ignored thermal energy, heat and temperature.

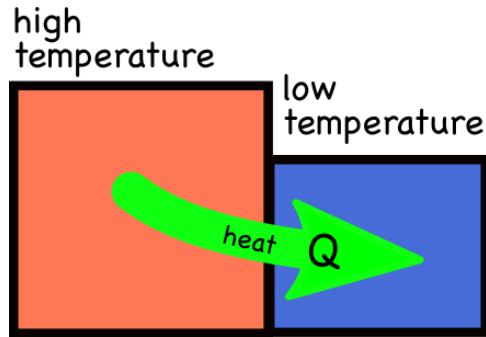Heat Q is the amount of thermal energy transferred from one system to another.

Figure 1: Transfer of energy or heat Q from one system at a higher temperature to another at a lower temperature.

Heat can be transferred in numerous ways, such as conduction, convection, and via absorption and emission of radiation.

When heat is transferred to an object, its temperature often goes up,

$$Q = C\Delta T$$

where C is the specific heat and ΔT is the change in temperature.

Heat is in units of energy. When an object is given heat, its total energy increases. The energy goes into various degrees of freedom such as raising atomic energy levels of atoms, raising vibrational and rotational levels of molecules, exciting phonons in solids and other types of waves, phase changes, ionization and increasing particle speeds.

While we have been measuring energy in Joules, heat is often measured in calories. 1 cal is the energy needed to increase 1 gram of water by 1° C at a pressure of 1 atmosphere. 1 cal = 4.184 J.

Temperature is measured in Kelvin or Celsius. To convert from Celsius to Kelvin, add 274.15°.

A useful constant is the Boltzmann constant,

$$k_B = 1.380649 \times 10^{-23} \text{J K}^{-1}$$

The quantity $k_B T$ is in units of energy and usually T is in units of Kelvin. The zero value in Kelvin has meaning as temperature cannot go below absolute zero.

To be more precise about what we mean by temperature we are going to start not with thermodynamics but with statistical physics.

1.2 Outline

A closed system has constant volume, energy, numbers of particles and constant values of external forces on it such as gravity.

We assume that a closed system is **equally likely** to be any of the quantum states that are accessible to it. This is the fundamental assumption underlying statistical mechanics.

Entropy measures the number of accessible states. If there are g accessible states then the **entropy** is

$$\sigma \equiv \ln g.$$

Conventional entropy S differs from σ by a factor of k_B.

A log is used in the definition for the entropy because the number of accessible states is usually really really large.

Because a closed system depends on its volume V, the total energy U and the numbers of particles N, the number of accessible states also depends on these quantities and so does the entropy.

Two isolated systems are brought in thermal contact with one another. The total energy remains constant but they may transfer energy from one system to the other. A closed system with more energy usually has more ways to partition the energy and so a larger number of possible states. The transfer of energy between the two systems increases the total number of states in the entire system. The total entropy of the entire system increases while the total energy remains fixed. The entropy increase occurs because the total system is most likely to be found in states with large multiplicity.

The combined system is in thermal equilibrium when the entropy is maximized. The derivative of entropy w.r.t. energy defines temperature. That way the two systems have the same temperature when equilibrium is reached.

A closed system in contact with a **thermal reservoir** with temperature T has probability of being in a particular state with energy ϵ that depends on the Boltzmann factor

$$e^{-\frac{\epsilon}{k_B T}}$$

where k_B is Boltzmann's constant.

The **Maxwellian velocity distribution**, the **Planck black body radiation spectrum** and the **ideal gas law** can be derived using statistical physics. The first two of these are derived using the Boltzmann factor.

Thermal and statistical physics connect the microscopic properties of a system with its bulk thermodynamic behavior.

That was the outline. Now we will go into detail on each piece of this story.

2   Counting States – Multiplicity functions

Each quantum state of a system has a definite energy. The **multiplicity** or *degeneracy g* is the number of states with the exact same energy. We define the entropy of a system as

$$\sigma = \ln g$$

The reason for the logarithm is that the multiplicity can be really really large. If we can count the number of accessible states of a system, then we know its entropy.

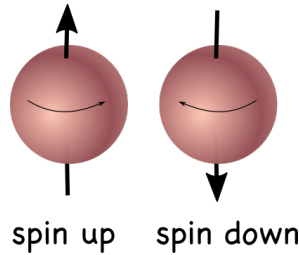## 2.1 Multiplicity function for binary spin systems

Figure 2: A particle that can have one of two possible energy states. We refer to the two possible states as spin-up and spin down.

We consider N particles. Each particle can be in one of two states. It is convenient to label the two states $\uparrow$ and $\downarrow$. The energy of a particle might not be the same in the $\uparrow$ state as the $\downarrow$ state. An example where this is true is electron spins in a magnetic field.

A state for 5 particles would look something like this

$$\uparrow_1\uparrow_2\downarrow_3\downarrow_4\uparrow_5$$

With N particles there are 2^N possible states.

All possible states can be found by evaluating the product

$$\Pi_{i=1..N}(\uparrow_i + \downarrow_i) = (\uparrow_1 + \downarrow_1)(\uparrow_2 + \downarrow_2)...(\uparrow_N + \downarrow_N)$$

For example if there are three particles

$$\Pi_{i=1,2,3}(\uparrow_i + \downarrow_i) = (\uparrow_1 + \downarrow_1)(\uparrow_2 + \downarrow_2)(\uparrow_3 + \downarrow_3)$$
$$=\uparrow_1\uparrow_2\uparrow_3 + \uparrow_1\uparrow_2\downarrow_3 + \uparrow_1\downarrow_2\uparrow_3 + \uparrow_1\downarrow_2\downarrow_3 + \downarrow_1\uparrow_2\uparrow_3 + \downarrow_1\uparrow_2\downarrow_3 + \downarrow_1\downarrow_2\uparrow_3 + \downarrow_1\downarrow_2\downarrow_3$$

Notice there is a single state where there are all up and a single state where they are all down. There are three states with two ups and one down and three states with two downs and ones up.

The total energy only depends on the total number of ups and the total number of downs, not upon which particles are up and which particles are down. For three particles we can count

$$(\uparrow + \downarrow)^3 = \uparrow\uparrow\uparrow + 3 \uparrow\uparrow\downarrow + 3 \uparrow\downarrow\downarrow + \downarrow\downarrow\downarrow$$

and the order of the spins does not matter. We can use the binomial expansion to compute the number of states for N particles

$$(x + y)^N = x^N + Nx^{N-1}y + \frac{1}{2}N(N-1)x^{N-2}y^2 + ... + y^N$$

$$= \sum_{t=0}^{N} \frac{N!}{(N-t)!t!}x^{N-t}y^t$$

Here t (going from 0 to N) is an integer index that is used to write the binomial coefficients. We shift the index from t to s with

$$t = s + \frac{N}{2}$$

giving us

$$(x + y)^N = \sum_{s=-N/2}^{N/2} \frac{N!}{(\frac{1}{2}N - s)!(\frac{1}{2}N + s)!} x^{\frac{1}{2}N-s} y^{\frac{1}{2}N+s}. \tag{1}$$

We assume that N is even so that s is a set of integers ranging from $-N/2$ to $N/2$. Whereas t goes from 0 to N and describes the number of spin-ups, the integer s is zero when there are the same number of spin-ups as spin-downs.

Rewriting the sum in terms of the up and down states

$$(\uparrow + \downarrow)^N = \sum_{s=-N/2}^{N/2} \frac{N!}{(\frac{1}{2}N - s)!(\frac{1}{2}N + s)!} \uparrow^{\frac{1}{2}N-s} \downarrow^{\frac{1}{2}N+s}. \tag{2}$$

The number of up spins and down spins in terms of the total number of particles and the integer s is

$$N_\uparrow = \frac{1}{2}N - s$$

$$N_\downarrow = \frac{1}{2}N + s. \tag{3}$$

We can compute the number of states with this number of ups and downs as

$$g(N, s) = \frac{N!}{(\frac{1}{2}N - s)!(\frac{1}{2}N + s)!} = \frac{N!}{N_\uparrow!N_\downarrow!} \tag{4}$$

Equation 2 can also be written

$$(\uparrow + \downarrow)^N = \sum_{s=-N/2}^{N/2} g(N, s) \uparrow^{\frac{1}{2}N-s} \downarrow^{\frac{1}{2}N+s}. \tag{5}$$

What does the distribution look like? If we divide by 2^N (which is the total number of states) then we have a probability distribution that is given by the coefficients of the binomial expansion. The number $2s$ can be considered a **spin excess** as it is the difference between the number of down spins and number of up spins. The spin excess

$$2s = N_\downarrow - N_\uparrow. \tag{6}$$

The number s is the number of spins above the mean that are down.

Suppose spins are set randomly. Then the probability of N particles having spin excess $2s$ is

$$p(s) = \frac{g(N, s)}{2^N}.$$

The normalization for the probability $\sum_s p(s) = 1$ follows because the multiplicity functions come from the binomial expansion (as in equation 5)

$$\sum_{s=-N/2}^{s=N/2} g(N, s) = 2^N.$$

If there is an energy difference between up and down spins caused by a magnetic field B then the total energy of the system is

$$U(s) = 2smB \tag{7}$$

where m is the magnetic moment of one spin. The multiplicity function $g(N, s)$ then lets us calculate the entropy for a particular energy state as a function of spin excess. Given U we can compute s (determining the spin excess) and this gives us multiplicity $g(N, s)$ and entropy $\ln g(N, s)$. Instead of using s we can write $g(N, U)$ and $\sigma(N, U)$ writing multiplicity and entropy in terms of energy instead of in terms of spin excess variable.

We do this on the problem set!

2.2 The sharpness of the multiplicity function for a binary spin system

The multiplicity of a system with N spins and spin excess $2s$ is

$$g(N, s) = \frac{N!}{N_\uparrow! N_\downarrow!}$$

(repeating equation 4 from above).

The entropy is the natural logarithm of the multiplicity

$$\begin{aligned} \sigma = \ln g(N, s) &= \ln \frac{N!}{N_\uparrow! N_\downarrow!} \\ &= \ln N! - \ln N_\uparrow! - \ln N_\downarrow! \end{aligned} \tag{8}$$

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2.2.1 Stirling's approximation

Stirling's approximation is an approximation for a factorial that is valid for large N,

$$\ln N! \approx \frac{1}{2}\ln 2\pi + \left(N + \frac{1}{2}\right)\ln N - N. \tag{9}$$

This can also be written as

$$N! \approx \sqrt{2\pi N}\left(\frac{N}{e}\right)^N$$

Stirling's approximation is often used in statistical mechanics. We use it to simplify our expression for the multiplicity function.

Because $N = N_\uparrow + N_\downarrow$

$$\ln N! \approx \frac{1}{2}\ln(2\pi) + \left(N + \frac{1}{2}\right)\ln N - N$$

$$\approx \frac{1}{2}\ln 2\pi + \left(N_\uparrow + \frac{1}{2} + N_\downarrow + \frac{1}{2}\right)\ln N - \frac{1}{2}\ln N - N_\uparrow - N_\downarrow$$

where we have used Stirling's approximation on the first line.

We approximate the other factorials in the multiplicity function in equation 8 using Stirling's approximation (equation 9)

$$\ln N_\uparrow! \approx \frac{1}{2}\ln 2\pi + \left(N_\uparrow + \frac{1}{2}\right)\ln N_\uparrow - N_\uparrow$$

$$\ln N_\downarrow! \approx \frac{1}{2}\ln 2\pi + \left(N_\downarrow + \frac{1}{2}\right)\ln N_\downarrow - N_\downarrow. \tag{10}$$

We subtract these from our expression for $\ln N!$ in equation 8

$$\ln g(N,s) \approx -\frac{1}{2}\ln 2\pi - \frac{1}{2}\ln N + \left(N_\uparrow + \frac{1}{2}\right)\ln\frac{N}{N_\uparrow} + \left(N_\downarrow + \frac{1}{2}\right)\ln\frac{N}{N_\downarrow}$$

$$\approx \frac{1}{2}\ln\frac{1}{2\pi N} - \left(N_\uparrow + \frac{1}{2}\right)\ln\frac{N_\uparrow}{N} - \left(N_\downarrow + \frac{1}{2}\right)\ln\frac{N_\downarrow}{N} \tag{11}$$

However, using equation 3 for $N_\uparrow$,

$$\frac{N_\uparrow}{N} = \frac{\frac{1}{2}N - s}{N} \approx \frac{1}{2}\left(1 - \frac{2s}{N}\right).$$

It is convenient to compute the Taylor series of the natural log for small x

$$\ln(1 + x) \approx x - \frac{x^2}{2}.... \tag{12}$$

To compute this series expansion we have used these derivatives

$$f(x) = \ln(1+x) \qquad f(0) = 0$$
$$f'(x) = \frac{1}{1+x} \qquad f'(0) = 1$$
$$f''(x) = -\frac{1}{(1+x)^2} \qquad f''(0) = -1$$

We use equation 12 to simplify the expression for the log of $N_\uparrow/N$ in equation 10

$$\ln \frac{N_\uparrow}{N} = \ln \frac{\frac{1}{2}N - s}{N}$$
$$= \ln \left[\frac{1}{2} \left(1 - \frac{2s}{N} \right) \right]$$
$$= -\ln 2 + \ln \left(1 - \frac{2s}{N} \right)$$
$$\approx -\ln 2 - \frac{2s}{N} - \frac{2s^2}{N^2} \tag{13}$$

Similarly using equation 3 for $N_\downarrow$,

$$\ln \frac{N_\downarrow}{N} = \ln \frac{\frac{1}{2}N + s}{N} \approx -\ln 2 + \frac{2s}{N} - \frac{2s^2}{N^2} \tag{14}$$

We insert equations 13 and 14 back into our expression for the multiplicity $\ln g(N, s)$ (equation 11)

$$\ln g(N,s) \approx \frac{1}{2} \ln \frac{1}{2\pi N} - \left(\frac{1}{2}N + s + \frac{1}{2} \right) \left(-\ln 2 + \frac{2s}{N} - \frac{2s^2}{N^2} \right)$$
$$- \left(\frac{1}{2}N - s + \frac{1}{2} \right) \left(-\ln 2 - \frac{2s}{N} - \frac{2s^2}{N^2} \right)$$
$$\approx \frac{1}{2} \ln \frac{1}{2\pi N} - \left(\frac{1}{2}N + \frac{1}{2} \right) 2 \left(-\ln 2 - \frac{2s^2}{N^2} \right) - 2s \left(\frac{2s}{N} \right)$$
$$\approx \frac{1}{2} \ln \frac{1}{2\pi N} + N \ln 2 - \frac{2s^2}{N} + ..$$

We rewrite this

$$g(N,s) \approx \frac{1}{\sqrt{2\pi N}} 2^N e^{-\frac{2s^2}{N}}. \tag{15}$$

Recall a normalized Gaussian function looks like this

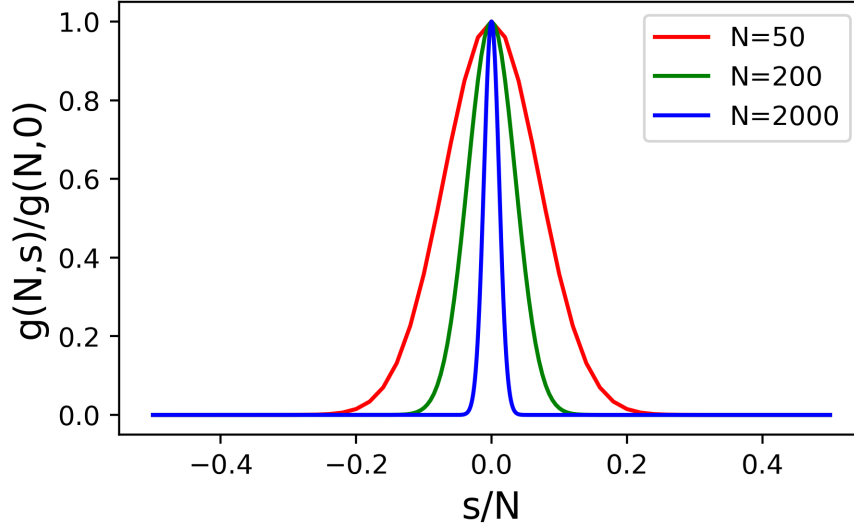$$\frac{1}{\sqrt{2\pi \sigma_g^2}} e^{-\frac{x^2}{2\sigma_g^2}}$$

Figure 3: The multiplicity function for a system of N particles with two states becomes taller and skinnier as N increases. For large N it is a good approximation to assume that the system is near the peak of the distribution.

where I am using σ_g for the standard deviation so as not to confuse it with σ for entropy. Notice that equation 15 resembles a Gaussian function!

With $s = 0$ equation 15 becomes

$$g(N, s = 0) = g(N, 0) \approx \frac{1}{\sqrt{2\pi N}} 2^N. \tag{16}$$

We notice that this gets large as N gets large. That means the peak of the function is very large as N increases. It is convenient to write

$$g(N, s) \approx g(N, 0) e^{-\frac{2s^2}{N}}. \tag{17}$$

How far in s do we need to go to get half the multiplicity of the peak? This happens when $s = s_h$ and

$$e^{-\frac{2s_h^2}{N}} \approx \frac{1}{2}$$

$$-\frac{2s_h^2}{N} \approx -\ln 2$$

$$\frac{s_h}{N} \approx \frac{1}{\sqrt{N}}$$

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The width of the peak divided by the largest possible width for s (which is $N/2$) shrinks as N increases.

The peak value becomes higher and narrower as N gets larger.

If all states are equally likely, then the system is less and less likely to ever be in a state distant from the most likely one. It is usually a **very** good approximation to assume that a large system is near the peak of the distribution.
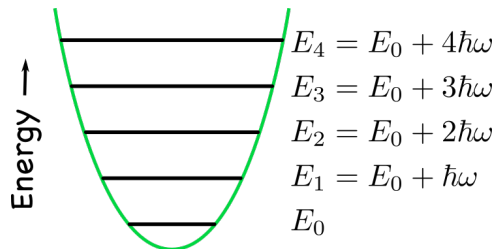
$$E_4 = E_0 + 4\hbar\omega$$
$$E_3 = E_0 + 3\hbar\omega$$
$$E_2 = E_0 + 2\hbar\omega$$
$$E_1 = E_0 + \hbar\omega$$
$$E_0$$

Figure 4: Energy levels of a quantum harmonic oscillator.

2.3 Multiplicity function for n quanta of energy and N harmonic oscillators

In the previous section we computed the multiplicity function of a system of N objects that can have two states. Now we look at a system of N objects that can have more than two states.

The quantum states of a harmonic oscillator have energy eigenvalues

$$\epsilon_s = s\hbar\omega + \text{constant}$$

where integer $s \geq 0$ refers to the quantum state.

Why is it useful to explore an ensemble of quantum harmonic oscillators? Harmonic oscillators are relevant in *many* physical models. Examples are phonons in solids and distribution of photons giving the black-body radiation spectrum.

We now consider N harmonic oscillators. We refer to i-th quantum state of the i-th oscillator as s_i. With N harmonic oscillators the total energy

$$\epsilon_n = \sum_{i=1}^{N} s_i \hbar\omega + \text{constant} = n\hbar\omega + \text{constant}$$
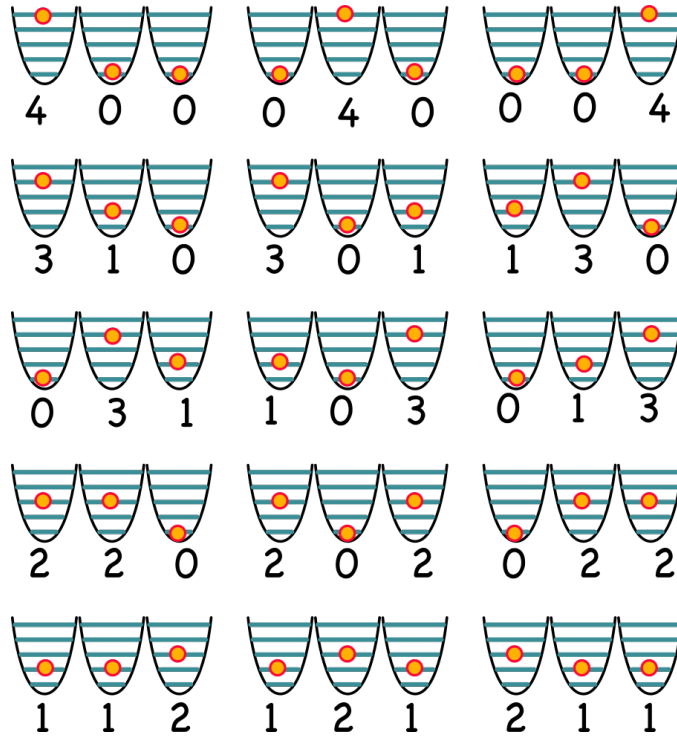
with

$$n \equiv \sum_i s_i$$

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Figure 5: Ways to distribute 4 quanta among 3 harmonic oscillators. In the top panel there are three ways one harmonic oscillator gets 4 energy quanta. In the second and third from top panels, there are 6 ways one oscillator gets 3 quanta and one oscillator gets 1 quantum. In the bottom two panels, there are three ways for two oscillators to get 2 quanta and three ways for 1 oscillator to get 2 quanta and two oscillators to get 1 quantum. The multiplicity is $g(N = 3, n = 4) = 15$.

the number of quanta of size $\hbar\omega$ that are distributed among the N harmonic oscillators.

We would like to compute the multiplicity function

$$g(N, n)$$

where N is the number of harmonic oscillators and n is the number of energy quanta of size $\hbar\omega$. Note that reviously we found $g(N, s)$ for a spin system with s setting the total energy. Here we find $g(N, n)$ with n setting the total energy.

First let's consider a single harmonic oscillator. If we have n quanta, then there is only one way we can distribute it. The one harmonic oscillator gets it all and its energy state must be ϵ_n. There only one way to distribute the energy with $N = 1$,

$$g(1, n) = 1$$

and the multiplicity is 1.

What if we have two harmonic oscillators ($N = 2$)? The first harmonic oscillator can get any number of quanta; $s_1 = 0, 1.....n$ quanta. Once that is chosen, the number of quanta that the second harmonic oscillator gets is exactly determined and is $s_2 = n - s_1$. So there are $n+1$ ways to chose the state. This is the same as the number of ways to chose the energy of the first harmonic oscillator.

$$g(2, n) = n + 1$$

What if we have three harmonic oscillators ($N = 3$)? The first one can get any number of quanta $s_1 = 0, 1, ...n$ quanta. The second one can get $s_2 = 0, 1, ...(n - s_1)$ quanta. The last one is completely determined and gets $n - s_1 - s_2$ quanta. We can chose s_1 in $n + 1$ ways, we can chose s_2 in $n - s_1 + 1$ ways and the last one is set from the first two.

$$
\begin{aligned}
g(3, n) &= \sum_{s_1=0}^{n} (n - s_1 + 1) \\
&= \sum_{i=0}^{n} (n + 1) - \sum_{i=0}^{n} i \\
&= (n + 1)^2 - n(n + 1)/2 \\
&= \frac{n^2 + 3n + 2}{2} = \frac{(n + 2)(n + 1)}{2}
\end{aligned}
$$

The examples for $N = 1, 2, 3$ we just computed are consistent with multiplicity function

$$g(N, n) = \frac{(N + n - 1)!}{n!(N - 1)!} \tag{18}$$

Below we will derive this relation.

For n energy packets and N oscillators, the multiplicity is equal to the number of unordered ways to make a sum of N non-negative integers that equals n. In number theory and combinatorics, a **partition** of a positive integer n, also called an **integer partition**, is a way of writing integer n as a sum of positive integers.

The problem of computing $g(N, n)$ is equivalent to finding the coefficient of x^n in the product

$$f(x) = (1 + x + x^2.....x^n)^N = \left(\sum_{i=0}^{n} x^i \right)^N \tag{19}$$

as we must chose a single term in each of the N factors. In other words the coefficient of x^n in $f(x)$ is equal to $g(N, n)$.

Why does this work? In the first factor, the exponent of the chosen term is equivalent to the number of quanta given to the first oscillator. Like wise for all the other factors.

The sum of the exponents of the chosen terms from each factor sum to n. Since the harmonic oscillators are interchangeable, it does not matter the order in which the factors are multiplied.

Consider $N = 2$ oscillators and $n = 2$ quanta. We compute multiplicity $g(2,2) = 3!/(2!1!) = 3$. These three states are the following: the first oscillator gets 2 quanta, the second oscillator gets two quanta and both oscillators each get one quanta. Note that this is not the same as randomly distributing 2 things in 2 bins which would have 4 in stead of 3 possibilities. Let's check that the partition calculation is sensible.

$$(1 + x + x^2)^2 = 1 + x^2 + x^4 + 2x + 2x^2 + 2x^3$$
$$= 1 + 2x + 3x^2 + 2s^3 + x^4.$$

The coefficient of x^2 is 3, consistent with $g(N = 2, n = 2) = 3$.

In equation 19, since terms with power greater than n don't contribute, the multiplicity $g(N, n)$ is is also equal to the coefficient of x^n in

$$g(x) = \left(\sum_{i=0}^{\infty} x^i \right)^N. \tag{20}$$

Since $g(N, n)$ is the coefficient of x^n in this sum

$$g(x) = \left(\sum_{i=0}^{\infty} x^i \right)^N = \sum_{n=0}^{\infty} g(N, n) x^n. \tag{21}$$

To find the coefficient of x^n in this sum it helps to know the geometric series

$$\sum_{i=0}^{\infty} t^i = \frac{1}{1 - t}$$

We notice that we can write

$$g(x) = \left(\sum_{i=0}^{\infty} x^i \right)^N = \left(\frac{1}{1 - x} \right)^N \tag{22}$$

We will take n derivatives of the right hand side of equation 21.
We will take n derivatives of the right hand side of equation 22.
We evaluate both sets of derivatives at $x = 0$.
We will set the two sets of derivatives to be equal to each other and solve for $g(N, n)$.

Now we take some derivatives. Starting with the right hand side of equation 22

$$g(x) = \left(\frac{1}{1-x} \right)^N$$

$$\frac{dg(x)}{dx} = \frac{N}{(1-x)^{N+1}}$$

$$\frac{d^2 g(x)}{dx^2} = \frac{N(N+1)}{(1-x)^{N+2}}$$

$$\frac{d^3 g(x)}{dx^2} = \frac{N(N+1)(N+2)}{(1-x)^{N+3}}$$

$$\frac{d^n g(x)}{dx^n} = \frac{N(N+1)...(N+n-1)}{(1-x)^{N+n}}$$

$$= \frac{(N+n-1)!}{(N-1)!} \frac{1}{(1-x)^{N+n}}$$

$$\left. \frac{d^n g(x)}{dx^n} \right|_{x=0} = \frac{(N+n-1)!}{(N-1)!}$$

Starting with

$$g(x) = \sum_{i=0}^{\infty} g(N,i) x^i$$

$$\frac{d^n g(x)}{dx^n} = \sum_{i \geq n}^{\infty} g(N,i) x^{i-n} \frac{i!}{(i-n)!}$$

$$\left. \frac{d^n g(x)}{dx^n} \right|_{x=0} = g(N,n) n!$$

The last expression follows because only one term remains, the one with $i = n$. Equating these two expressions for $\left. \frac{d^n g(x)}{dx^n} \right|_{x=0}$ together we find

$$g(N,n) = \frac{(N+n-1)!}{n!(N-1)!} \tag{23}$$

as we stated above.
Also see the following links:
Ways to write N as a sum of non-negative integers.
What is a partition? (Number theory)
   A comment. We have been sloppy about keeping track of the ground state energy level. It is okay to neglect the ground state energy when computing multiplicity. However, it does affect probabilities computed using the Boltzmann factor.
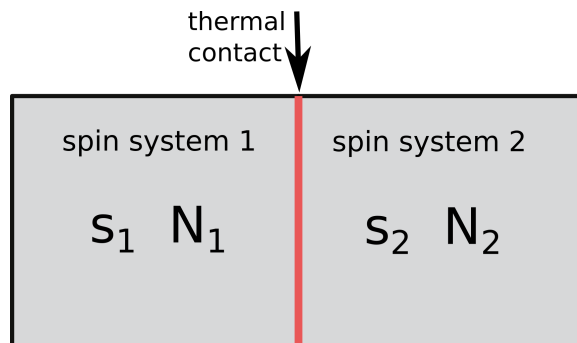
3 Entropy and Temperature

Figure 6: Two binary spin systems in thermal contact. The system on the left has numbers of particles N_1 and spin excess $2s_1$. The system on the right has numbers of particles N_2 and spin excess $2s_2$.

3.1 Two spin systems in thermal contact

In a previous section we computed the multiplicity of a binary spin system. For a spin system with N spins that can either be up or down, the multiplicity function (equation 4)

$$g(N, s) = \frac{N!}{(\frac{1}{2}N - s)!(\frac{1}{2}N + s)!} \approx g(N, 0)e^{-\frac{2s^2}{N}}$$

with

$$g(N, 0) = \frac{1}{\sqrt{2\pi N}} 2^N$$

Here $2s$ is the spin excess and s is the number of down spins above $N/2$.

We consider two initially isolated spin systems, one with s_1 and N_1 and the other with s_2, N_2 (as illustrated in Figure 6).

With fixed N_1, N_2, s_1, s_2 what is the multiplicity of the combined system? For each state in the first system we have $g(N_2, s_2)$ states in the second system. The multiplicity of the combined system is the product of the multiplicities for each system,

$$g_1(N_1, s_1)g_2(N_2, s_2) = g(N_1, 0)g(N_2, 0) \exp\left(-\frac{2s_1^2}{N_1} - \frac{2s_2^2}{N_2}\right). \tag{24}$$

The spin excess parameter of the total system $s = s_1 + s_2$. Replacing $s_2 = s - s_1$

$$g_1(N_1, s_1)g_2(N_2, s - s_1) = g_1(0)g_2(0)\exp\left(-\frac{2s_1^2}{N_1} - \frac{2(s - s_1)^2}{N_2}\right)$$

$$\ln(g_1(N_1, s_1)g_2(N_2, s - s_1)) = \ln(g_1(0)g_2(0)) - \frac{2s_1^2}{N_1} - \frac{2(s - s_1)^2}{N_2}$$

The spin excess $2s$ of the total system gives the energy of the total system. This must be fixed if the total energy for the combined system is constant. The spin excess of the first system (s_1) can still vary. A variation in s_1 corresponds to an exchange of energy between the two spin systems. The previous equation shows the multiplicity of two isolated systems. When they are put in thermal contact they can exchange energy.

What value of s_1 gives a maximum total entropy for the combined system? Maximum total entropy states are the ones that are most likely! This would be the more likely s_1 value after the two systems are allowed to exchange energy. To find the extremum of the total entropy for the combined system we take the derivative w.r.t. s_1 and set it equal to zero

$$\frac{\partial}{\partial s_1}\ln(g_1(N_1, s_1)g_2(N_2, s - s_1)) = -\frac{4s_1}{N_1} + \frac{4(s - s_1)}{N_2} = 0$$

This is zero when

$$\frac{s_1}{N_1} = \frac{s - s_1}{N_2} = \frac{s_2}{N_2}$$

Let $\hat{s}_1, \hat{s}_2$ be values that satisfy this relation. These are values for the spin excess of the individual systems that maximize the total multiplicity of states for the combined system and so are most likely when the two systems are in thermal contact.

$$\frac{\hat{s}_1}{N_1} = \frac{s - \hat{s}_1}{N_2} = \frac{\hat{s}_2}{N_2}$$

Relating these to s for the full system (we solve for $\hat{s}_1, \hat{s}_2$)

$$\hat{s}_1 = s\frac{N_1}{N}$$

$$\hat{s}_2 = s\frac{N_2}{N} \tag{25}$$

With these ratios we can compute the multiplicity function again using equation 24

$$(g_1 g_2)_{max} = g_1(0)g_2(0)e^{-\frac{2\hat{s}_1^2}{N_1} - \frac{2\hat{s}_2^2}{N_2}}$$

$$= g_1(0)g_2(0)e^{-2s^2\frac{N_1^2}{N^2 N_1} - 2s^2\frac{N_2^2}{N^2 N_2}}$$

$$= g_1(0)g_2(0)e^{-\frac{2s^2}{N^2}(N_1 + N_2)}$$

$$= g_1(0)g_2(0)e^{-\frac{2s^2}{N}}$$

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This is the maximum possible multiplicity for excess s.

Let's take the system very slightly out of equilibrium and estimate some really large numbers. Let $s_1 = \hat{s}_1 + \delta$ and $s_2 = \hat{s}_2 - \delta$. Using equation 24, equation 25 and our definition for $(g_1g_2)_{max}$, the multiplicity just slightly out of equilibrium is

$$g(N_1, \hat{s}_1 + \delta)g(N_2, \hat{s}_2 - \delta) = g_1(0)g_2(0)e^{-\frac{2s_1^2}{N_1} - \frac{2s_2^2}{N_2}}$$

$$= g_1(0)g_2(0)e^{-\frac{2s^2}{N}}e^{-\frac{2\delta^2}{N_1} - \frac{2\delta^2}{N_2}}$$

$$= (g_1g_2)_{max}e^{-\frac{2\delta^2}{N_1} - \frac{2\delta^2}{N_2}}$$

Take $N_1 = N_2 = 10^{22}$ as in Avogadro's number. Take $\delta = 10^{12}$ which seems large but not as a fraction $\delta/N_1 = 10^{12-22} = 10^{-10}$.

$$\frac{2\delta^2}{N_1} = \frac{2 \times 10^{24}}{10^{22}} = 200$$

We estimate the multiplicity

$$\frac{g(N_1, \hat{s}_1 + \delta)g(N_2, \hat{s}_2 - \delta)}{(g_1g_2)_{max}} = e^{-\frac{4\delta^2}{N_1}} = e^{-400} = 10^{-174}$$

This is a *very* small number. That means the probability is extremely small that δ would ever be this large. It's extremely unlikely that the system would be this far from the maximum multiplicity state.

In summary, when two systems are in thermal contact they can exchange energy or heat. The combined system moves to its most probable state. This state has maximum multiplicity and so has maximum entropy for the combined system. To reach this state, the two systems exchange energy. Once it reaches the maximum entropy state, the combined system is in equilibrium.

3.2 Thermal equilibrium

We now look at two systems in thermal contact but with a total constant energy shared between them. The setting is just like described in the previous section except we will not just look at spin binary systems, but any two closed idealized systems that are in thermal contact. The first system has number of particles N_1 and energy U_1 and the second system has number of particles N_2 and energy U_2. The total number of particles is $N = N_1 + N_2$ and the total energy is $U = U_1 + U_2$.

The multiplicity of the combined system

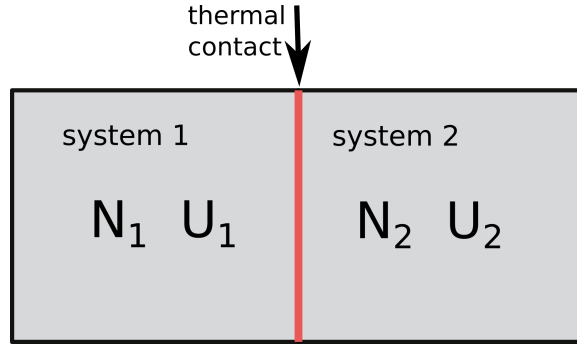$$g(N, U) = \sum_{U_1} g_1(N_1, U_1)g_2(N_2, U - U_1)$$

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Figure 7: Two generic closed systems in thermal contact. The first system has number of particles N_1 and energy U_1 and the second system has number of particles N_2 and energy U_2.

where I have written this in terms of a sum over all possible U_1 values. The system is most likely to be near a state with the largest multiplicity. This is an extremum with variation in multiplicity $dg = 0$, but we are keeping N_1, N_2, U fixed. Starting with

$$g(N, U_1 + U_2) = g_1(N_1, U_1)g_2(N_2, U_2)$$

$$\begin{aligned} dg &= \left(\frac{\partial g_1(N_1, U_1)}{\partial U_1}\right)_{N_1} g_2(N_2, U_2)dU_1 + g_1(N_1, U_1)\left(\frac{\partial g_2(N_2, U_2)}{\partial U_2}\right)_{N_2} dU_2 \\ &= \left(\frac{\partial g_1}{\partial U_1}\right)_{N_1} g_2 \, dU_1 + g_1\left(\frac{\partial g_2}{\partial U_2}\right)_{N_2} dU_2 = 0 \end{aligned} \tag{26}$$

at the extremum. The subscripts of N_1 and N_2 mean that we are holding them fixed when we take the derivative.

With total energy conserved

$$dU_1 + dU_2 = 0.$$

We replace dU_1 with $-dU_2$ in equation 26 and find that

$$\frac{1}{g_1}\left(\frac{\partial g_1}{\partial U_1}\right)_{N_1} = \frac{1}{g_2}\left(\frac{\partial g_2}{\partial U_2}\right)_{N_2} \tag{27}$$

at the extremum. It is useful to show that for a function $f(x)$

$$\frac{d\ln f(x)}{dx} = \frac{1}{f(x)}\frac{df(x)}{dx}. \tag{28}$$

This lets us write the previous relation as

$$\left(\frac{\partial \ln g_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \ln g_2}{\partial U_2}\right)_{N_2}. \tag{29}$$

We define **entropy** as
$$\sigma(N, U) \equiv \ln g(N, U)$$
The values of entropy giving a maximum in the multiplicity of the total or combined system
$$\left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2} \tag{30}$$
When U_1 and U_2 satisfy this condition then the entropy of the total system system is a **maximum**.

Energy is no longer transferred between the two subsystems when the systems are in **equilibrium**, or equivalently equations 29 and 30 are satisfied and entropy is a maximum in the combined system. We **define the temperature** so that the temperatures of each subsystem is the same when they reach equilibrium,
$$\frac{1}{T} \equiv k_B \left(\frac{\partial \sigma}{\partial U}\right)_N$$
with k_B the Boltzmann constant.

The temperatures of the two subsystems
$$(k_B T_1)^{-1} = \left(\frac{\partial \ln g_1}{\partial U_1}\right)_{N_1}$$
$$(k_B T_2)^{-1} = \left(\frac{\partial \ln g_2}{\partial U_2}\right)_{N_2}.$$
If $T_1 > T_2$ then energy is transferred from the first system to the second system to achieve equilibrium. While this is happening the total **entropy increases**.

When the two subsystem temperatures are equal, then the entropy is maximum, and we say the combined system is in **equilibrium**.

So far we have defined entropy as the log of the multiplicity or number of states accessible to a system. In classical thermodynamics the conventional entropy S is defined as
$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N \tag{31}$$
The two entropy functions are related by
$$S = k_B \sigma \tag{32}$$

Conventional entropy S is in units of k_B which is in units of energy/temperature. The entropy σ is unitless.

Let's look again at our definition for temperature
$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N$$

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For small changes in energy U we can write this as

$$\frac{1}{T} = \frac{dS}{dU}$$
$$dU = TdS. \tag{33}$$

The change in energy is related to the change in entropy and with slope given by the temperature. With two systems in thermal contact and not exchanging anything but energy, dU is the energy transferred between the two systems. The energy

$$Q = TdS \tag{34}$$

is also called **heat**.

Two systems in thermal contact are in **thermal equilibrium** if they have the same temperature and are no longer exchanging energy. A combined system in thermal equilibrium is a maximum entropy state.

3.3 Two systems of harmonic oscillators in thermal contact

We consider two systems with different numbers of harmonic oscillators and let them exchange energy. That's another way of saying that they are in thermal contact. The initial energy of the system with N_1 oscillators is U_1 and the number of states is

$$g_1 = g(N_1, U_1).$$

Its entropy is

$$\sigma_1 = \ln g_1(N_1, U_1).$$

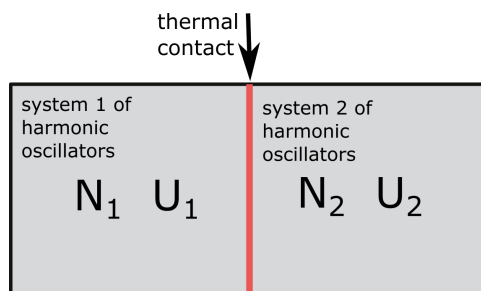The other system has entropy

$$\sigma_2 = \ln g_2(N_2, U_2).$$

Figure 8: Two systems of harmonic oscillators in thermal contact. The first system has number of oscillators N_1 and total energy U_1 and the second system has number of oscillators N_2 and energy U_2. The multiplicity functions are computed using equation 23.

As the total energy is fixed

$$U = U_1 + U_2.$$

However the total entropy

$$\sigma = \sigma_1 + \sigma_2 = \ln g_1 + \ln g_2 = \ln(g_1 g_2) = \ln\left[g_1(N_1, U_1) g_2(N_2, U_2)\right]$$

is not fixed as energy is exchanged between the two systems. Notice that the multiplicities multiply but the entropies add.

The entropies are functions of the number of energy quanta that go into one of the systems as energy is conserved; $\sigma_1(U_1)$ and $\sigma_2(U - U_1)$. At equilibrium the derivative of the entropy w.r.t to U_1 is zero because entropy is a maximum

$$\frac{d(\sigma_1 + \sigma_2)}{dU_1} = 0$$

$$\frac{d\sigma_1}{dU_1} + \frac{d\sigma_2}{dU_1} = 0$$

Because $U_2 = U - U_1$, at equilibrium

$$\frac{d\sigma_1}{dU_1} + \frac{d\sigma_2}{dU_1} = \frac{d\sigma_1}{dU_1} - \frac{d\sigma_2}{dU_2} = 0$$

$$\frac{d\sigma_1}{dU_1} = \frac{d\sigma_2}{dU_2}$$

At equilibrium, the derivative of the entropy of the first system w.r.t to its total energy is equal to the derivative of the entropy of the second system w.r.t to its total energy.

The temperature of a system is defined as

$$\frac{1}{k_B T} \equiv \frac{d\sigma}{dU} \tag{35}$$

When the entropy is maximized, the temperature of the two systems are equal,

$$\frac{d\sigma_1}{dU_1} = \frac{d\sigma_2}{dU_2} = \frac{1}{k_B T}.$$

Why is the entropy for the total combined system maximized? It is maximized because the total system is most likely to be found with energy distributed in a state with maximum multiplicity.

We have introduced the concept of **thermal equilibrium**. When two initially isolated systems at different temperatures are brought into thermal contact, they are not in thermal equilibrium. After their temperatures become equal they are in thermal equilibrium. Thermal equilibrium for the combined system is that of maximum entropy.
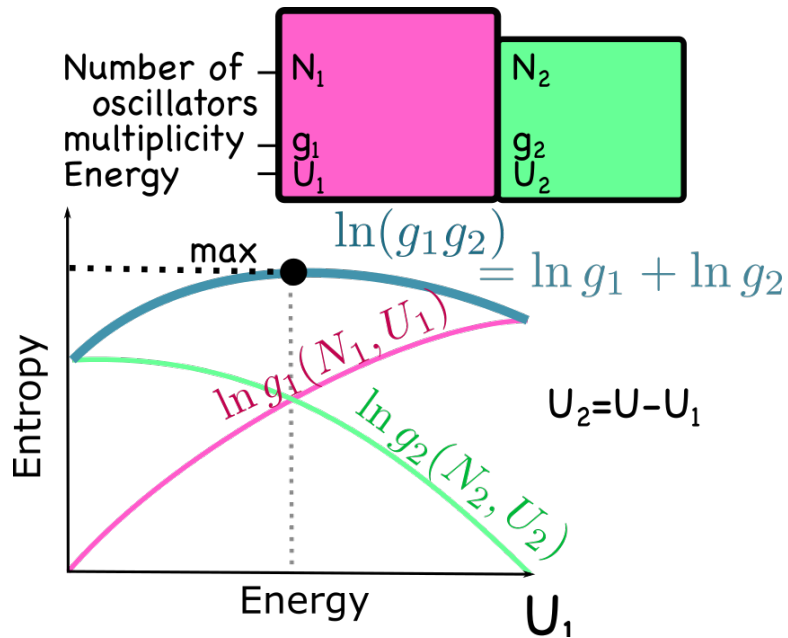
Figure 9: Two systems of harmonic oscillators in thermal contact. The vertical axis is entropy. The horizontal axis is energy. The pink curve is the entropy of the larger system of harmonic oscillators as a function of U_1, the energy of the same system. The total energy $U = U_1 + U_2$ is fixed. The green curve is the entropy of the smaller system as a function of U_1. The sum of the entropies $\ln g_1 + \ln g_2 = \ln(g_1 g_2)$ is the blue curve. When the entropy is maximized, the two systems are in thermal equilibrium. The entropies are computed from the multiplicity functions using equation 23.
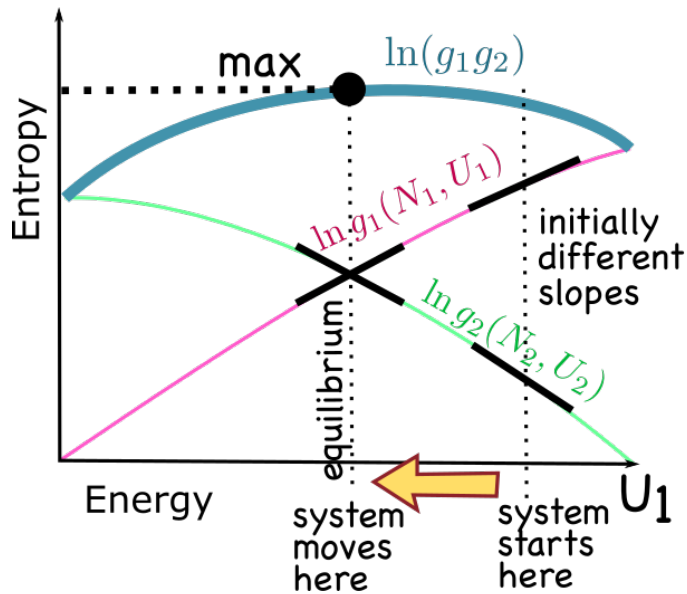
Figure 10: The two systems of harmonic oscillators are initially at different temperatures and have different magnitude slopes on this plot. The temperature depends on the slope! Initially $\frac{1}{k_B T_1} = \frac{\partial \sigma_1}{\partial U_1}$ and $\frac{1}{k_B T_2} = \frac{\partial \sigma_2}{\partial U_2} = -\frac{\partial \sigma_2}{\partial U_1}$. Then the two systems are brought into thermal contact. When the entropy is maximized the two systems are in thermal equilibrium. At this temperature T, the slopes are equal magnitude and opposite sign; $\frac{1}{k_B T} = \frac{\partial \sigma_1}{\partial U_1} = -\frac{\partial \sigma_2}{\partial U_1}$. Energy moves from the higher temperature system to the other one until their two temperatures are the same.

3.4 An example of a change in entropy

We take a 10g piece of copper at $T = 350°$ K and put it in contact with another 10g piece of copper at $T = 290°$ K. The specific heat of copper is about $C = 0.39$ J g^{-1} K^{-1}. Heat flows from the hotter piece to the colder piece of copper. The final temperature is T_f.

$$\Delta U = mC\Delta T = 10\text{g} \times 0.39\text{J g}^{-1}\text{K}^{-1}(T_f - 290) = 10\text{g} \times 0.39\text{J g}^{-1}\text{K}^{-1}(350 - T_f)$$

$$T_f = \frac{1}{2}(290 + 350)\text{K} = 320\text{K}$$

The temperature changes are ± 30K.

The change in energy

$$\Delta U_2 = -\Delta U_1 = 10 \times 0.39\text{J K}^{-1}(320 - 290)\text{K} = 117\text{J}$$

This amount of energy goes from the hotter copper piece to the colder one.

What is the change in entropy just after contact when only 0.1 J has been exchanged?

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N$$

We rewrite this as

$$dS = \frac{dU}{T}$$

This relation can also be written as heat $Q = TdS$.

The entropy of the first piece is decreased by

$$dS_1 = \frac{-0.1\text{J}}{350\text{K}} = -2.86 \times 10^{-4}\text{J K}^{-1}$$

We use the initial temperature of the warmer piece as we are estimating the change in entropy just after the two systems are put in thermal contact. The entropy of the second copper piece is increased by

$$dS_2 = \frac{0.1\text{J}}{290\text{K}} = 3.45 \times 10^{-4}\text{J K}^{-1}$$

and we have used its initial temperature. The total entropy change is

$$dS_1 + dS_2 = (-2.86 + 3.45) \times 10^{-4} = 0.6 \times 10^{-4}\text{J K}^{-1}$$

We notice that the total entropy has increased! In fundamental units the total increase in entropy is

$$\Delta\sigma = \frac{S}{k_B} = \frac{0.6 \times 10^{-4}\text{J K}^{-1}}{1.4 \times 10^{-23}\text{J K}^{-1}} = 0.4 \times 10^{19}$$

The entropy change is related to the multiplicity of states before and after the thermal contact,

$$\Delta\sigma = \sigma_{after} - \sigma_{before} = \ln \frac{g_{after}}{g_{before}}$$

The multiplicity of states has increased by a multiplicative factor

$$e^{\Delta\sigma} = e^{0.4\times 10^{19}}$$

which is *very* large.

Did the total entropy locally in the lab increase? Yes.

Did the total energy locally in the lab increase? No.

(Trying not to integrate over the universe because it has infinite volume. Also the universe expands and cools as it expands. Entropy still increases).

4 The laws of thermodynamics

Thermal equilibrium has the same meaning as a state of maximum entropy.

- Zeroth law. If two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other. This follows from equality of temperature.

- First law. Heat is a form of energy.

- Second law. The total entropy of an isolated or closed system can never decrease over time. Isolated systems spontaneously evolve towards thermodynamic equilibrium, the state with maximum entropy.

- Third law. The entropy approaches a constant value as temperature goes to zero.

The third law deserves some discussion. If there is a single state with minimum energy then the multiplicity at zero temperature is 1 and the entropy is zero. However, the minimum energy state may not be non-unique and that gives a finite entropy at zero temperature. Zero temperature has meaning despite the fact that $T^{-1} = \frac{d\sigma}{dU}$ goes to infinity as $T \to 0$.

4.1 Ways to increase entropy

Rather than characterize entropy as a kind of disorder, we have quantitatively related it to the multiplicity of states.

Entropy can also be considered the logarithm of the amount of **information** needed to describe a system.

When considering the multiplicity we can try to understand why different operations tend to increase entropy.

Here are some operations that tend to increase entropy of a system.

- Add particles

- Add energy

- Increase the volume. (More deBroglie wavelengths fit in the box).

- Decompose molecules into atoms (disassociation)

- Mixing

- Let a linear polymer curl up

- Ionization

- Melting, evaporation, sublimation

When counting the multiplicity of systems with constant energy, the setting is sometimes called the **microcanonical ensemble**.

5   Summary

The multiplicity function is the numbers of ways to distribute energy among particles and energy states in a system.

Entropy σ is the natural logarithm of the multiplicity function g.

$$\sigma = \ln g$$

The multiplicity function for N spins with $N_\uparrow = \frac{1}{2}N - s$ and $N_\downarrow = \frac{1}{2}N + s$ is

$$g(N, s) = \frac{N!}{(\frac{1}{2}N - s)!(\frac{1}{2}N + s)!} = \frac{N!}{N_\uparrow! N_\downarrow!}$$

Here $2s$ is the spin excess.

The multiplicity of N quantum mechanical harmonic oscillators with n energy quanta is

$$g(N, n) = \frac{(N + n - 1)!}{n!(N - 1)!}$$

This is the number of ways to distribute n quanta among the N oscillators.

Stirling's approximation for large factorials is often useful in statistical mechanics.

$$\ln N! \approx \frac{1}{2}\ln 2\pi + \left(N + \frac{1}{2}\right)\ln N - N.$$

Using Stirling's approximation, the multiplicity function for a binary spin system is approximately Gaussian in shape near the peak at $s = 0$,

$$g(N, s) \approx g(N, 0)e^{-\frac{2s^2}{N}}$$

When two closed systems are brought into thermal contact, the total entropy is maximized. This is equivalent to the assumption that all states (with the same total energy) are equally likely, therefor the types of states that have the highest multiplicity (and so giving highest entropy) are the most likely.

Temperature is defined with a derivative of entropy w.r.t to energy.

$$\frac{1}{k_B T} = \left(\frac{\partial \sigma(N, U)}{\partial U} \right)$$

or

$$\frac{1}{T} = \left(\frac{\partial S(N, U)}{\partial U} \right)$$

Both derivatives keep things like volume and number of particles fixed. Here conventional entropy $S = k_B \sigma$. This definition for temperature implies that when two system in thermal contact are at the same temperature, the multiplicity of states (and entropy) for the entire system is maximized. This also implies that energy will flow from the higher temperature system to the lower temperature system if the temperatures are not the same. This also implies that entropy tends to increase. For small changes in energy, the heat $Q = dU$ and

$$Q = TdS$$

and this is consistent with our definition for temperature.

A system in thermal equilibrium is one at maximum entropy. The second law of thermodynamics states that the entropy of a closed or isolated system can never decrease.