Lesson 2: Temperature

Notes from Prof. Susskind video lectures publicly available on YouTube

Units of temperature and entropy

Let's spend a few minutes talking about units, in particular the Boltzmann constant k_B, a question about which last chapter ended with.

What is the Boltzmann constant? Like many constants in physics, k_B is a conversion factor.

The speed of light is a conversion factor from distances to times. If something is going at the speed of light, and in a time t covers a distance x, then we have

$$x = ct \tag{1}$$

And of course if we judiciously choose our units, we can set $c = 1$.

Typically these constants are conversion factors from what we can call human units to units in some sense more fundamental. Human units are convenient for scales and magnitudes of quantities which people can access reasonably easily.

We haven't talked about temperature yet, which is the subject of this lesson. But let's also say something about the units of temperature, and see where k_B – which will simply be denoted k when there is no possible confusion – enters the picture. Units of temperature were invented by Fahrenheit[1] and by Celsius[2], in both cases based on physical phe-

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[1]Daniel Gabriel Fahrenheit (1686 - 1736), Polish-born Dutch physicist and engineer.

[2]Anders Celsius (1701 - 1744), Swedish physicist and astronomer.

nomena that people could easily monitor.

The units we use in physics laboratories nowadays are Kelvin[3] units, which are Celsius or centigrade degrees just shifted by an additive constant, so that the 0 °C of freezing water is 273.15 K and 0 K is absolute zero. There is no lower temperature.

Thus temperatures Kelvin are relative to absolute zero, while temperatures centigrade are relative to the freezing point of water at atmospheric pressure, as chosen by Celsius. And the centigrade scale, the unit of 1 degree, was simply set by dividing the temperature scale between freezing and boiling of water at atmospheric pressure, into 100 units.

All these choices were highly arbitrary. Fahrenheit used a mixture of water, ice and amonium chloride for his 0 °F, which turned out to be -17.78 °C. Alcohol or anything else could have been used. It would have produced different units.

The point is that these were units which people could manipulate. They could measure temperatures. It is not too hard to measure a change in temperature of one degree centigrade with a human scale thermometer. By human scale I mean an object that you can make in your shop. So the centigrade scale is a human construct that was invented for convenience.

In the XIXth century, it was not fully understood – although

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[3]William Thomson, aka lord Kelvin (1824 - 1907), Irish-born British physicist.

Kelvin may have understood it – that the real physical units which temperature has to do with is energy. Temperature is really an energy. For example, the temperature of a gas determines the kinetic energy of its molecules.

And one measure of the temperature of the gas is just the kinetic energy of the molecules. Well, you might say: wait a minute, that is not so good because if the gas is a composite of two gases, say oxygen and helium, the molecules of which have quite different masses, surely they have different kinetic energy. But they don't! We will eventually prove that in thermal equilibrium at a given temperature, all of the particles in a gas have basically the same kinetic energy.

In fact if you suspended a bowling ball into into a gas, or even a liquid, when the thermal equilibrium is reached, and everything is at the same temperature, the kinetic energy of the bowling ball would be exactly the same as the kinetic energy of one molecule of the gas.

That seems a little bit odd. But when you think about it, it is not that odd. If the bowling ball has the same energy as a molecule, it would surely move a lot slower than a single molecule, for the reason that its mass is much larger. If mv^2 for the bowling ball is the same as mv^2 for a molecule, then obviously a much bigger m will lead to a much smaller v.

The main point is that temperature is really a measure of an amount of energy. So the natural units for temperature are really those of energy.

But at the time when temperature first started to be mea-

sured, nobody could measure a molecule[4]. After the atomic hypothesis appeared, under the impetus of people like Dalton[5], nobody had the vaguest idea how massive molecules were, or how much energy a typical molecule had at a given temperature. And in fact, until the time of Maxwell[6], Stefan[7] and Boltzmann, nobody had the idea that temperature could have to do with the energy of a basic constituent. So the scale of temperatures was defined before there was a notion that temperature so to speak equals energy.

The natural unit for temperature could be Joules[8] for example. A Joule is a fine unit of temperature, although a rather large one. Indeed the typical energy of a single molecule in thermal equilibrium at room temperature is a very tiny number of Joules. And the temperature is essentially the kinetic energy of one molecule. Pay attention to the fact that temperature is not an additive quantity. If we take two volumes of gas, both at the same temperature, and put them together we still have the same temperature. So we are indeed talking about the temperature of *one* molecule.

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[4]In fact in the XVIIIth century nobody knew about molecules. The atomic hypothesis emerged progressively in the early XIXth century as a nice although crazy explanation for the fact that chemical reactions always involved simple ratios of quantities of reactants. Without entering into the details – and there are many! –, if you put 1 liter of oxygen and 3 liters of hydrogen together to make water, you will indeed get water but you will be left with 1 liter of unused hydrogen. If you put 1 liter of oxygen and 1 liter of hydrogen, you will be left with 1/2 liter of unused oxygen.

[5]John Dalton (1766 - 1844), English chemist.

[6]James Clerk Maxwell (1831 - 1879), Scottish physicist.

[7]Josef Stefan (1835 - 1893), Austrian physicist.

[8]Standard unit of energy named after James Prescott Joule (1818 - 1889), English brewer and physicist.

The conversion factor between human units and the basic units of energy is therefore a very small number. To figure it out, let's start with the relationship between the energy E of a single molecule in a dilute gas and its temperature T. We consider a dilute gas because we don't want to worry too much about the energies of interaction between the molecules. The formula is

$$E = \frac{3}{2} \, k_B \, t_K \qquad (2)$$

The 3 is easy to understand. It has to do with the number of dimensions in space. A molecule has a kinetic energy from moving along the x-axis, the y-axis and the z-axis. So there is a factor of 3. And the half is just a glitch of definition.

The temperature t_K in equation (2) is the *human scale temperature*, expressed in degrees Kelvin. And k_B is the Boltzmann constant, that is the conversion factor. In that case it has units of energy divided by degrees Kelvin. And it is a rather small number as you might expect.

If the temperature is room temperature, t_K is about 300 degrees K. The energy E of a single molecule, on the other hand, is clearly very small. So k_B (read k Boltzmann) is necessarily very small. Its numerical value is

$$k_B \approx 1.4 \text{ x } 10^{-23} \quad \frac{m^2 \, kg}{s^2 \, K} \qquad (3)$$

$kg \, m^2/s^2$ is a unit of energy. It is of course a Joule, and it is the standard unit of energy in the MKS system of units.

K is the abbreviation for degrees Kelvin.

It is no accident that Avogadro's number[9] is of order of magnitude 10^{23}.

Finally equations (2) and (3) give for the kinetic energy of a molecule in a gas at 300 °K

$$E = 6.2 \text{ x } 10^{-21} \ J \tag{4}$$

As explained above, it is striking that this energy doesn't depend on the kind of molecule. Whether big or small, the molecule will have the same kinetic energy.

For a given type of molecule we can calculate its speed. Let's take, for instance, a molecule of nitrogen. It is made of two nitrogen atoms. One nitrogen atom is made of 7 protons, 7 neutrons and 7 electrons. Its mass is $m \approx 2.3 \text{ x } 10^{-26} \ kg$. Thus writing $1/2 \ mv^2 = E$, and solving for v, we get for the speed of a nitrogen molecule

$$v = 5.2 \text{ x } 10^2 \ m/s \tag{5}$$

In other words, when we feel cozy at room temperature and ordinary pressure, it is because billions of billions of tiny molecules of nitrogen keep hitting us at a speed of about 520 meters per seconds[10].

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[9]Avogadro's number is 6.02 x 10^{23}. Under ordinary conditions of temperature and pressure it is the number of particles in a volume of gas of 22.4 liters.

[10]At freezing temperature their speed is still about 500 meters per second, since it varies like the square root of the temperature expressed in degrees Kelvin.

The main point about equation (2) is that the fundamental quantity of interest involved, namely t_K, always comes in multiplying the Boltzmann constant. This is just because the fundamental quantity is really energy. So we define a new measure of temperature

$$T = k_B \ t_K \tag{6}$$

This measure is the Boltzmann constant multiplying the human temperature. It has units of energy. Once we use this measure T we get rid of k_B in all equations involving temperature. We will never see it again.

But we must remember that what from now on we call temperature, namely T, differs from thermometer temperature. It is thermometer temperature (expressed in degrees Kelvin) multiplied by an extremely small conversion factor.

That same factor k_B is also present in the units of entropy. Remember what entropy is: it is a unit of information. It is measured in bits.

Entropy was discovered as an interesting quantity, which always increases, by a young steam engineer and scientist by the name of Carnot[11], who was working in the 1820's on improving the recently invented steam engines.

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[11]Sadi Carnot (1796 - 1832), French military engineer and physicist. His father, French mathematician and leading revolutionary figure Lazare Carnot (1753-1823), also did significant work on energy and machines. One of Sadi Carnot's nephews, also named Sadi Carnot, become president of the French republic at the end of the XIXth century.

Carnot had a quantity, defined in terms of temperatures and energies and so forth, which wasn't easily measured, but played an important role in describing theoretically the functioning of steam engines. He did not know anything about the underlying microscopic phenomena driving his quantity, let alone its relation to a probabilistic description of our ignorance of the exact state of the system. At the time of Carnot, understanding the relationships between the concepts of temperature, heat, and work was still incipient. The name *entropy* was given only by Clausius[12] in 1865. And statistical thermodynamics was created by Boltzmann even later.

Entropy received the notation S. For the moment let's use S_{carnot} for the measure discovered by Sadi Carnot. That is the quantity which he did not call entropy but whose variation, at a given temperature, he understood, was equal to the variation of energy divided by the temperature[13].

S_{carnot} has units. It is energy divided by temperature. If the temperature is measured in Kelvin then it is Joule per Kelvin. In other words, Joule per Kelvin was Carnot's units of entropy.

But in modern physics we think of entropy as being measured in bits. A fundamental unit of entropy is logarithm of 2 for example. And that is dimensionless.

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[12]Rudolf Clausius (1822 - 1888), German physicist.

[13]In *Réflexions sur la puissance motrice du feu et sur les machines*, 1824, Carnot wrote: The motive power of heat is independent of the agents employed to realize it; its quantity is fixed solely by the temperatures of the bodies between which is effected, finally, the transfer of caloric.

So there is a conversion factor again. Carnot's unit of entropy differs from what we have called entropy up to now. Let's recall what entropy is from a statistical point of view. We have some probability distribution over a discrete set of states, figure 1.
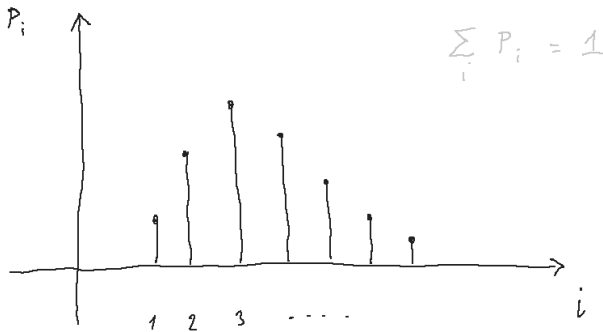

Figure 1: Probability distribution over a discrete set of states.

Then we define the entropy S – without the subscript Carnot now – as

$$S = -\sum_i P_i \, \log P_i \tag{7}$$

It is the same as equation (27) of last chapter. It is a rough measure of the logarithm of the number of states which are important under the statistical distribution above. That is what we called entropy.

What is the connection between Carnot's entropy, and Boltzmann's entropy given by equation (7)? They are simply related by the Boltzmann constant

$$S = \frac{1}{k_B} \, S_{carnot} \qquad (8)$$

In other words when Carnot's entropy is an ordinary number like 6 in a steam engine, Boltzmann's entropy is enormous. It is roughly proportional to the number of molecules in the system.

Once we know how to go back and forth between human units of temperature or human units of entropy and the more fundamental units of temperature and entropy – for temperature it is energy, and for entropy it is a dimensionless quantity – then we no longer need to use Boltzmann constant. With fundamental units, the Boltzmann factor effectively goes out of all of our equations.

Conversely, if for some reason we need to go back to human units, it is easy to reintroduce. Whenever you see capital T and you want to get it into human units think of it as k_B times temperature in Kelvin. And whenever you see an entropy S which has a huge value typically, and you want to get it into steam engine units multiply it by k_B.

Questions / answers session

Question: From equation (2), apart from the factor 3/2, now temperature is in Joules?

Answer: It depends of course now on what unit of energy you are using on the left-hand side.

If you are using the Joules for your units of energy, then the temperature T will be in Joules. And in three dimensions a particle of energy 10 Joules, will have a temperature of about 7 Joules. To be rigorous we should speak of "Joules-of-temperature" such that 0.67 Joule-of-temperature is the same as 1 ordinary Joule. Then we would say that a particle of 10 Joules of energy has a temperature of about 7 Joules-of-temperature.

The point is that it is not really new units. It is just like measuring something in units of 1.5 meters. Although purists would maintain that it is a new unit.

What is the Joule? It is the unit of energy in MKS units, that is meters, kilograms and seconds units. 1/2 Joule is the energy of a 1 kg object moving at a velocity of 1 m/s.

Q.: k Boltzmann is always 1.4 x 10^{-23} ?

A.: k Boltzmann is always a constant. But its numerical value depends on the units you are using. The same is true of the speed of light, or of any physical constant. We like to use units of length and time such that $c = 1$, because is more convenient than its expression in meters per second. And it is much more convenient that its expression, for example, in knots[14]. But nothing prevents us from using knots if we like.

The customary value of 1.4 x 10^{-23} for Boltzmann constant is only when it is measured in Joules per Kelvin. If

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[14]Nautical unit of speed. 1 knot = 1 852 meters per hour.

you use, say, BTU per whatever measure of temperature you like, you will get a different numerical value.

If instead of using Kelvin units we used Fahrenheit units (with the zero shifted to correspond to absolute zero, though), the numerical value of k_B would change.

Energy itself, like mass or length or many other characteristics of objects in nature, is a quantity with units. Therefore you have to specify what units you are talking about.

When I say temperature has units of energy, it does. But you have to pick your units of energy.

If you are working in the meter kilogram second set of units, then your natural unit of energy is called the Joule. It is not a new unit. It is the name of the unit of energy in MKS units. It is just $kg\ m^2/s^2$.

And that is the unit that you would use for temperature if you want to keep your formulas simple[15].

You could use any nice units you like, electron-volts or Planck masses or whatever. If you change your units of energy, then you change your units of temperature, with still the ratio $E = 3/2\ T$. But, to keep simple formulas, your units of temperature and energy should be kept consistent.

Boltzmann's entropy on the other hand is dimensionless. The quantity $-\sum_i P_i\ \log P_i$ doesn't have units. Carnot's

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[15]With the caveat that 1 Joule = 0.67 "Joules-of-temperature". Or said another way, if $T = 1$ then $E = 1.5$.

entropy has units, since it is related to Boltzmann's with the multiplicative factor k_B in equation (8).

We could also defend the point of view that degrees Kelvin are really units of energy. Then k_B would be viewed as dimensionless, which doesn't mean that it does not depend on units. Anyway we look at it, it is just a conversion factor.

Q.: Is the value of $k_B \approx 1.4$ x 10^{-23} J/K something determined experimentally?

A.: Yes, it is.

Boltzmann himself, as Newton, never knew the value of his own constant. I don't mean the usefulness, I mean the actual numerical value.

That is because nobody had measured the properties of atoms, the masses of atoms to any accuracy, until Einstein came along and figured out how to do it. Boltzmann died just before the value of his constant was known.

I'm quite sure, though, that he had a rough idea. And he certainly knew that it was connected to Avogadro's number. But he probably never knew with any precision what the value of his number was. The same is true of Newton.

Boltzmann did understand that, if only he could measure the properties of atoms, then energy could be measured using temperature and his constant. That he understood.

Alright, thus far we have not said what temperature is. It is time we turn to it.

What is temperature?

We have an intuitive sense of temperature. That is because when we touch a hot thing it does something to our nerve cells and so forth and so on. And we have a natural intuition about hot and cold.

But temperature is a rather derived mathematical quantity. It begins with the twin notions of energy and entropy.

We will eventually define precisely what it means for a system to be in thermal equilibrium. But, until we do so, it just means intuitively that a system, closed or exchanging with the outside, has been allowed to evolve for a long enough time that it just settles down to some equilibrium configuration. However, as we shall see in a moment, even in equilibrium it is still evolving at a microscopic level between many states.

As said, it may be closed, or it may be exchanging with the environment. If the environment is not changing with time the system under consideration will equilibrate in a certain sense that will become clear.

During the process of equilibration, energy may flow from the system to the environment. In that case we say the system is hotter than the environment. The energy may also flow in the other way on the average, in which case we

say that the system is colder than the environment. And in equilibrium on the average energy is flowing neither way.
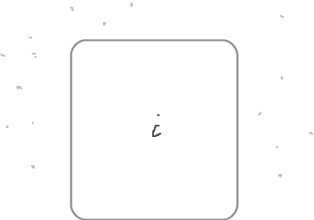
Let's consider a system in equilibrium, figure 2.

Figure 2: System in equilibrium with its environment. The system is in state i.

The system inside the box has a lot of degrees of freedom. They define the collection of states[16]. The i-th state has an energy E_i.

Now, when a system comes to equilibrium it doesn't come to a particular state i. It is interacting with its environment. Energy is going back and forth. Complicated things are happening.

Even in equilibrium there is some probabilistic process going on over time. At time t, there is some probability that the system be in the i-th state, which has energy E_i. So there is a probability $P(i)$ attached to the i state. For lightness of notation, we will just denote it P_i. And it doesn't

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[16]In lesson 1, we presented the full-fledged framework of probabilities [$\mathcal{E}$, Ω, P]. The various elements of Ω were the states denoted, when they were countable, ω_1, ω_2, etc. Now we refer to them simply by their label i.

depend on t, so we may forget about t for the moment.

The probabilities P_i's satisfy some rules. First of all, of course, they are positive and

$$\sum_i P_i = 1 \tag{9}$$

Secondly – it is not a rule but a definition –, the average energy of the system is

$$\sum_i P_i \, E_i \ = \ <E> \tag{10}$$

This is the average energy of the system when it is in equilibrium. When we say average what we really have in mind is that the energy is constantly changing. It fluctuates. Some extra energy goes out into the environment, and then it comes back in and so forth. So it is constantly fluctuating.

When the system is in equilibrium, at any time t, when averaged over a short period of time around t, the average energy over the possible states is a constant which doesn't depend on t, and equation (10) is the equation for this average energy.

And finally we have a notion of entropy.

$$S = -\sum_i P_i \, \log P_i \tag{11}$$

Now what is the probability distribution P_i? What does it depend on? Among other things, but mostly, it depends on

the average energy in the system.

The average energy may depend on the nature of the environment. If the environment is very hot, the average energy in the box may be high. If the environment is cold the average energy in the box may be low.

In other words, the environment determines the collection of states the system in equilibrium can be in, and their probability. It also determines the E_i's and therefore $< E >$, which we will simply denote E.

The average energy E of the system can be thought of as a parameter. For instance we can change the average energy of a kettle of water by putting it on a stove. Or we can cool it down but putting it out in the snow.

So we can change the average energy. In that sense the collection of states with non zero probability and the distribution of probability depends on E. So we will denote the probabilities as

$$P(i, \ E) \tag{12}$$

For every given average energy, in thermal equilibrium, there is a distribution of probability $P(i, \ E)$.

Of course if we increase the average energy E, then we shift and reshape of the probability distribution toward larger energy values of E_i's.

That means that there is not a single probability distribution P_i, that we call equilibrium, there is a family of them

indexed by the value of the average energy E. A given E corresponds to a given distribution $P(i, E)$, and conversely, figure 3.

On the horizontal axis are arranged the states i's in ascending order of energy E_i[17].
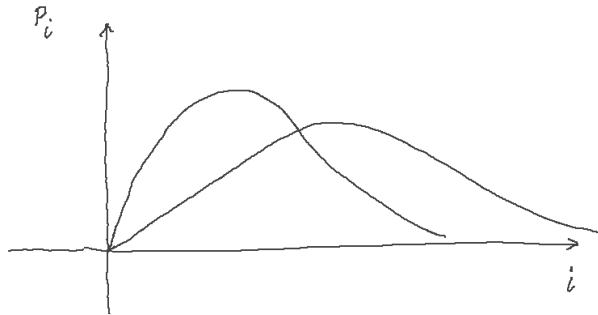

Figure 3: Two probability distributions corresponding to different average energies.

Which distribution corresponds to more average energy? Answer: the one that is peaked further out to the right.

We haven't calculated yet what is the distribution $P(i, E)$ for a given E. That will be one of our objectives. So far, all we can say is that *as a matter of experience* for each value E of the average energy there is a probability distribution. This forms altogether a family of probability distributions, two of them being represented on figure 3.

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[17]Of course, two states can have the same level of energy, but we can still arrange them so that the energies are growing toward the right.

Every probability distribution $P(i, E)$ satifies the three rules above: sum equal to 1, average energy equal to $< E >$, or E, and it has some entropy S.

We mentioned in chapter 1, that when talking about probabilities one must be totally clear about what is the experiment $\mathcal{E}$ we have in mind, that can be – at least in theory – reproduced, and whose outcome will change from replication to replication, and is therefore driven by a probability measure. So before proceeding, let's remind the reader what it is here.

We consider a system in thermal equilibrium. The theoretical experiment $\mathcal{E}$ is this: look at the system at time t, and suppose we have the power to observe everything about the system, in particular the position and velocity of every particle[18]. We call that state of the system ω_i, or simply i. That state has an energy E_i, which is a random variable, since E_i depends on ω_i and will vary from replica to replica. To reproduce $\mathcal{E}$ means to look again at a new time later, and so forth, supposing the system always remains in the *same* thermal equilibrium.

If we reproduce $\mathcal{E}$ a very large number of times, from the law of large numbers we can determine the distribution of probability over the possible states of the system. These are the $P(i, E)$. The average energy E is the following concept derived from experience: in thermal equilibrium the system can exchange with the outside; some energy goes back and

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[18]Of course quantum mechanics prevents that, but it allows knowing x and p up to the constraint $\sigma_x\ \sigma_p \geq \bar{h}/2$ and that degree of precision is quite sufficient for our purpose.

forth; but, averaged over even very short periods of time, the average energy doesn't change. So it is a characteristic of the system in thermal equilibrium. It is the E we are talking about above. It is also a characteristic of the probability distribution attached to the thermal equilibrium we are observing.

A note on terminology: the outside which somehow stabilizes the system in thermal equilibrium is often called a *heat bath.* The intuitive idea is that it will help the system reach the same temperature as the outside, while that of the outside doesn't change. Hence the term heat bath.

Of course, there are many probability distributions that we could write down that have the same average energy E. Where are we getting this one parameter family $P(i, E)$ from? That will come later. As a matter of experience if we know the average energy of a system, then there is some probability distribution, over the possible states it can take, associated with it. To give it a name, it is the Boltzmann distribution. It will be the subject of chapters 3 and 4.

For now we are just doing a mathematical exercise. We have a one parameter family of probability distributions, parameterized by the average energy. No two of them have the same average energy by assumption. And the higher the energy is, of course intuitively the broader the probability distribution in figure 3 is likely to be. And we will take that as a given.

To answer the question of some students about whether two states could be correlated, notice that the concept of correlation doesn't apply to our setting. Correlation is a

technical term with a very precise meaning. It is relevant when we consider *two random variables measured on the same experiment.* Here so far we measure only one, namely the energy E_i.

General speaking, the idea that one state could be correlated to another state reflects a confusion. In a random experiment $\mathcal{E}$, two measurements, one after the other, of any random variable X by definition are independent. To establish it, we would have to define a new experiment $\mathcal{F}$ which consists in performing $\mathcal{E}$ twice in a row, and we would have to define a probability measure for $\mathcal{F}$. But this probability measure would – by definition of how $\mathcal{F}$ is constructed – be the product of the probability measures for each of the replications of $\mathcal{E}$. So there is no meaningful notion, in our present setting, of two states being correlated. The reader is referred to any elementary probability manual to refresh his or her knowledge on this.

A more meaningful question would be what happens if there is more than one state with exactly the same energy – not average energy E, but E_i and E_j being the same. What if, say, E_1, E_7, and E_{36} are exactly the same? Well, first of all it never happens, but even if it did it would not raise any particular problem in the circumstances. Degeneracy, which means equal energy for different states, is a very rare and unusual thing. And, anyway, we don't have to worry about it.

For instance in figure 3, where on the horizontal axis the states are arranged with increasing energy E_i, we can assume that every state i has its own energy E_i, and every energy E_i has its own state i. If that makes things clearer,

let's take it as a working assumption.

Let's emphasize: the i-th state is the precise microscopic description of the system. It is the knowledge that an all-powerful, all-knowing observer would have. Every molecule, position and velocity, or whatever it takes to describe the exact microscopic state of the system is specified in the i-th state.

The fundamental idea of statistical mechanics is that, at a time t, the system is in one and only one precise state, but we – real life observer – have only an incomplete knowledge of it. Our incomplete knowledge is modeled with a probabilistic framework. We know that the system is in one of a collection of occupied states. And we know the probability distribution P, or $P(i)$[19] over them. The implicit random experiment $\mathcal{E}$ underlying our incomplete knowledge is a replication of the whole experiment leading to a measurement at the same time t. As we saw, what can change is the precise initial conditions, as well as the precise time t given by our timepiece.

We label the possible states i's in ascending order of the energy E_i. And for simplicity, we take it as given that no two states have exactly the same energy – which is typically true except in very unusual situations. So we have a clear notion of what we mean by i. We have a notion of what we mean by a distribution of probability P. And there is

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[19]We use indifferently the notation P, or $P(i)$, or $P(i)$'s, for the *whole distribution* of probability. The notation $P(i)$, or $P(i)$'s, for the whole collection may be a bit confusing, but it is standard practice. It means implicitely that i runs over its range of values. Sometimes of course, we do want to talk about one specific probability value of one i. But the context should always make it clear.

a one-to-one correspondence between an average energy E and a probabilitity distribution P, in a family of probabilitity distributions[20]. Thus E can be viewed as a parameter labeling the distributions in a family of probability distributions. That is why we use the notation $P(i,\ E)$ for the distribution of probability corresponding to E.

The nature of $P(i,\ E)$, which is the distribution of probability corresponding to a thermal equilibrium with average energy E, will become clear when we work out the Boltzmann distribution in chapter 4. Before that, our objective in the present chapter is to explain temperature.

Each distribution of probability in the family labeled by E has its own entropy. So the entropy becomes a function of E

$$S(E) = -\sum_i P(i,E) \log P(i,E) \qquad (13)$$

The entropy, which is a feature of a given probability distribution, now becomes a function of the average energy because for each average energy we have a different probability distribution[21].

So that tells us that there is a connection between entropy and energy *if we know the one parameter family* suggested in figure 3. And, as we said, we will discuss later where this

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[20]Not to be confused with the collection of possible states corresponding to *one* probability distribution.

[21]Furthermore, even though there are counterexamples, it is usually true that the relation between energy and entropy, for a given system, in the family of distributions we are concerned with, is one-to-one and increasing.

family of distributions comes from.

Having linked entropy and energy, now we can ask an interesting question.

Energy, entropy and temperature

Consider each one of the probability distributions, parametrized by a given average energy, figure 4. The higher the average energy, the more they will spread out to the right.
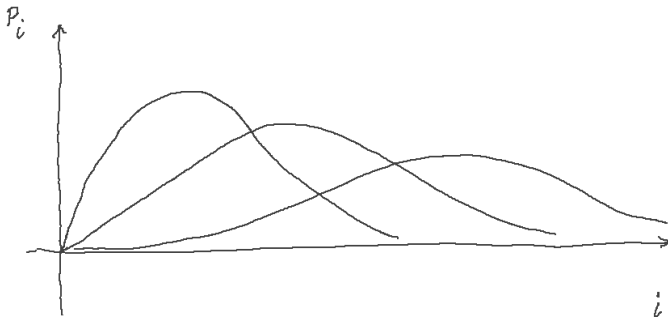

Figure 4: Family of probability distributions corresponding to different average energies.

We can ask: how much do we have to change the average energy in order to change the entropy by one bit or by a small amount ΔS?

To start with we can write the following identity from elementary calculus

$$\Delta E = \frac{\partial E}{\partial S}\, \Delta S \qquad (14)$$

This assumes nothing more than that energy and entropy are smooth functions that can be differentiated.

Equation (14) says that the change in the energy, in going from one probability distribution to the next, is the derivative of the energy with respect to the entropy times of change in the entropy.

We can also write it in the alternate and equivalent way

$$\Delta S = \frac{1}{\frac{\partial E}{\partial S}}\, \Delta E \qquad (15)$$

Incidentally, we write partial derivatives because in some problems there might be more than one variable to keep track of. But here there is no difference with ordinatry derivatives, and we could write dS/dE instead of $\partial S/\partial E$.

So far equations (14) and (15) are trivial. There is nothing insightful in them. We just look at the variation of the energy when we vary the entropy, or equivalently the variation of entropy when we vary the energy. By the way one over $\partial E/\partial S$ is nothing more than $\partial S/\partial E$.

If we want to know for example how much do we have to shift the energy – that is go the a probability distribution further to the right or further to the left – in order to change the entropy by one bit, then we would just stick in for ΔS one bit, namely $\log 2$, in equation (15). That would tell us how much energy ΔE it takes to change the entropy by one

bit.

Of course there is nothing special about 1 bit, all we want is to consider a *small change* in S and the related small change in E.

The main point is that the rate of variation

$$\frac{\partial E}{\partial S} = T \qquad (16)$$

is called *temperature.*

The temperature is the rate of variation of the energy with respect to the entropy. Or equivalently, 1 over temperature is the rate of variation of the entropy with respect to the energy. It is the more customary way to write it:

$$\Delta S = \frac{\Delta E}{T} \qquad (17)$$

And this is the formula we see most frequently in classical thermodynamics books. We even often see it written with human temperature and Carnot units of entropy, but as explained below it is equivalent, see equation (20).

We can also rewrite equation (17) with T upstairs, and drop the Δ's for d's instead. Then we have

$$dE = T \ dS \qquad (18)$$

As we said, temperature is a highly derived quantity. Even

though it is quite intuitive for us humans, in thermodynamics, be it classical or statistical, it is not a fundamental concept like entropy or energy, but a derived one, namely the rate of variation of the latter with respect to the former.

Equations (17) or (18) tell us that the higher the temperature, the more energy it takes to change the entropy. Conversely at low temperatures, on an absolute scale where zero is the absolute zero, a small change in energy produces a big change in entropy.

In equations (17) or (18) the temperature T is the modern measure of temperature in physics. If we switch to the human temperature t_K, measured in Kelvin, and to Carnot measure of entropy, equation (18) becomes

$$dE = t_K \ dS_{carnot} \qquad (19)$$

To see that, simply observe that $T = k_B \ t_K$, equation (6), and $S = S_{carnot}/k_B$, equation (8). If we introduce those in equation (18), the Boltzmann constant cancels and it yields equation (19), or equivalently

$$dS_{carnot} = \frac{dE}{t_K} \qquad (20)$$

which is essentially what Carnot wrote in 1824.

He didn't have to know about Boltzmann constant because it cancels in going from (18) to (19), or from (17) to (20).

We mention this because if you go and read a book on standard thermodynamics, you may wonder what happened to the constant k_B? It cancels out in the definition. And

equation (20) is the same as equation (17).

We have reached our objective of defining temperature. It is an odd and abstract definition. It is not in the least clear what equations (17) or (18) have to do with temperature as we experience it. So let's see now what it has to do with our ordinary idea of temperature.

We are going to assume that entropy is a monotonic increasing function of energy. That means that temperature, as defined in equation (17), is positive. $dS/dE > 0$ by assumption for the moment.

This means that when we increase the parameter E in the family of distributions represented in figure 4, we spread the distribution over a larger number of states i, and more specifically its entropy increases. We are going to prove most of these things, but let's take them as given for now.

So the question is: how is this definition of temperature in any way related to the familiar concept of temperature?

Link with the familiar concept of temperature

What is the familiar concept of temperature? Of course we are familiar with how things can be hot, tepid, cold, etc. We burn ourselves when we touch something too hot. But can we do something that is more physics oriented?

The definition of ordinary temperature which comes closest to being general has to do with how two systems can

exchange energy. And it will actually be a measure of the difference in their temperatures.

Consider two systems connected as in figure 5. And for simplicity let's suppose that the global system formed by the two of them is isolated.

Figure 5: Two systems which can exchange energy, but weakly.

We have system A and system B, connected by a thin pipe enabling them to exchange energy with each other, but only weakly. Little bits of energy can go back and forth between them and cause the energies to fluctuate. But on the average each one has an energy.

Imagine them having started out *not in contact*. They each were in equilibrium, at different temperatures T_A and T_B. These are the abstract temperatures defined in the preceding section. It is the rate of change of energy with respect to entropy in each system[22]. So each one of the boxes in figure 5 has been prepared with a given temperature by

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[22]Temperature is the slope of E as a function of S. Therefore, when the temperature is high, it takes a lot of energy to increase entropy by a little bit.

whatever it takes to make them have whatever temperature they have.

Now connect them. This simply means allowing them to interact with each other and exchange energy back and forth.

Which way does the energy flow?

In the ordinary concept of temperature, heat will flow from hot to cold. In other words energy will go from the system of higher temperature to the system of lower temperature. Now let's prove that this is also true with our abstract definition of temperature. This will establish the link between ordinary temperature and the abstract definition we gave.

Suppose $T_B > T_A$. Then we will show that heat will flow from B to A. We will also show that if $T_B = T_A$ then heat flows neither way. Heat means energy now, and we use the two terms indifferently for the time being.

A very important assumption we will also make is the *second law of thermodynamics*. Later on we will prove it, but for the moment let's take it as a postulate or a given. The second law of thermodynamics says that the entropy of an isolated system, left to itself to evolve over time, can only increase or at best stay the same[23].

More specifically, in the case of the two boxes in figure 5 that have been prepared separately in thermal equilibrium,

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[23]Remember that entropy is a measure of the incompleteness of *our knowledge* of the exact state of the system. So the second law says that we will know less and less well in what state the system is. Or, at best, the incompleteness of our knowledge will stay the same.

the second law of thermodynamics says that if we connect them, and let the global system to equilibrate again, heat will flow one way or another, until it eventually comes to some sort of compromise equilibrium. But the entropy will have increased.

Let's now follow the line of reasoning showing that T_A and T_B are consistent with ordinary temperature. The total entropy of the system is

$$S = S_A + S_B \tag{21}$$

Why is entropy additive? It comes from the mathematics. If you have two independent systems and each one has some sort of probabilistic description, the probability for the whole system to have some property multiplies. If you take the logarithm of probabilities it adds. That is essentially why entropy is additive.

A second useful fact is that when the system equilibrates by exchanging energy the total energy is conserved. This is the *first law of thermodynamics*. So if the energy of A increases then the energy of B decreases by the same amount. Or, written with an equation, we have

$$dE_A = -dE_B \tag{23}$$

Equivalently, the total change in energy of A and B is equal to zero.

Next, the second law of thermodynamics says that

$$dS_A + dS_B > 0 \tag{24}$$

Entropy increases. Let's stress that it is something we will need to justify.

Finally, for each box equation (18) holds, namely

$$dE_A = T_A \ dS_A$$
$$dE_B = T_B \ dS_B$$

(25)

This section is taken up and completed in lesson 3.