

PROFESSOR: Einstein's argument, we consider again our atoms. And this time we're going to use the thermal equilibrium. We're going to really make use of that fact.

So, again, we have level b and level a. And this is Einstein's argument.

And we're going to have no populations. If we discuss equilibrium, we can consider a system in a box. And there's a few billion atoms. And there's some atoms whose electron is going to be in state b. Some atoms whose electrons are going to be in state a. Let's call these numbers N_b and N_a . And we also have photons at temperature T and have a beta parameter 1 over the Boltzmann constant times T .

So this is the process we're going to consider. So what's going to happen? If we came up from the edition that we've built from 806, we would think, OK, there's going to be absorption process and stimulated emission process. And between the two, they're going to be able to reach equilibrium. We don't believe this is not a process that can equilibrate. So this would be our intuition.

The intuition for people that lived at the beginning of last century was rather different. They felt that there would be absorption process and there was spontaneous emission. The thing that you probably intuitively would think, if you are at a high level, you spontaneously decay. So the thing that was not known to them was this stimulated emission. That is what Einstein is credited for discovering here.

People felt, and I think the paper finds that makes clear that the intuition, is that you have spontaneous emission, in which spontaneously by some kind of instability, the higher state goes to the bottom. And you have absorption. But then Einstein figured out that you couldn't achieve equilibrium in that way.

Well, the way we're going to do it, we're going to put the two things we know-- the absorption and the stimulated emission-- and see that we don't get it to work, the equilibrium. But then when we add the spontaneous emission, we will. And as it turns out, the spontaneous emission is a little harder to calculate. If we were to do it in 806, it probably would be a matter of two lectures involving an electromagnetic field. So we will not do it. But the good thing is that Einstein's argument tells you the speed of spontaneous emission, the rate of spontaneous emission, in terms of this rate of stimulated emission or absorption. So it does the calculation

for you by some other thermodynamical means.

So we're going to use here three facts. One is that the-- three facts-- one is the populations are in equilibrium. So \dot{N}_a is they stop changing is equal to 0. And \dot{N}_b is equal to 0. They don't stop changing because nothing happens. All the time there will be emission, and there will be absorption. But if you reach equilibrium, the number of atoms remain the same on every state. So that's our statement that the populations achieve equilibrium.

The second statement is that the equilibrium is thermodynamical. So it's thermal equilibrium. That is N_b over N_a , for example, is the Boltzmann factor $e^{-\beta E_b}$ over $e^{-\beta E_a}$. And this is equal to $e^{-\beta (E_b - E_a)}$. You get $e^{-\beta (E_b - E_a)}$. So that's thermal equilibrium.

And the last thing that we need is a statement about the photons. What do they do when they have equilibrium? And that was known already due the work of Planck and others, black body equilibrium. So we need to know something about the thermal radiation.

And the way one describes this is in terms of a function U of ω $d\omega$. In the black body radiation, there are at a given temperature, there are photons with very little energy. There are some largest number of photons with some energy associated with temperature, and then it decays. So you have photons of all energy.

So if you want a description of what's going on in black body radiation, you can consider the energy in the photons in the frequency range. But you even must be more precise. It is the energy per unit volume in a frequency range. Because if it's different, the energy of the black body cavities, this room or it's a little box. So it's an energy per volume per frequency range. And that's what this quantity is.

So let me write it. Energy per unit volume in the frequency range $d\omega$. In other words, it's kind of a proxy for the number of photons available. All the photos have at some value of the frequency, of energy $e\omega$. So if you know the energy, you basically are getting here the number of photons with frequency ω in that range per unit volume, all that stuff.

So this has a formula. And the formula that was known to people was this quantities and then $\omega^3 d\omega$, over $e^{-\beta (E_b - E_a)}$. So this is the basis of the calculation.

What do we do? We have to consider the possible processes. OK, so our processes are absorption. And in this case, we go from a to b. And let's try to write a rate for them.

So what would the rate depend on? Well, here's some little assumptions. Certainly, if you don't have particles in the a state, you cannot have this process. So this process, the total rate that we observe in the box will depend on n_a . The more particles you have in this state a, the larger the probability that you get the transitions, and the larger the rate.

It will also be affected by the number of photons available at that frequency that can produce a transition in proportional to that. And finally, the quantity that our study of perturbation theory will tell us about, but at that time, finds that was not known, it's a transition coefficient, B_{ab} , he called it.

And this is the unknown one. And this is what we don't know. We know U . We assume we know n_a . This is the transition rate per atom and then multiplied by the number of atoms. So this is transition rate per atom.

Then we have the process of spontaneous emission. And then we will be another coefficient, B_{ba} . And it would depend on the number of particles that are in the state b, because spontaneous emissions that transition from b to a. We call it-- oh, not spontaneous stimulated. I'm sorry-- stimulated emission. This is the one we're considering. It's stimulated by the radiation. So it's also proportional to the number of photons present and proportional to the number of atoms that can be convinced to do the transition times another coefficient, B_{ba} .

So this is, I think, what we in 806 would do. We would consider this two processes and attempt to make it work. And let's see what we get then.

We're trying to get equilibrium. So we want the transitions to equilibrate and, therefore, the populations not to change. So let's look-- for example-- you could look at either one, but you can look at \dot{n}_b . It should be 0. But it's equal to the rate of absorption minus the rate of stimulated emission.

You see because the number of particles in b change because you get some new particles in state b due to the absorption process. And it happens with this rate. And you lose some particle because some atoms do the transition from the higher level to the lower level.

So what is the rate of absorption? We have it here. It's this one, $B_{ab} U \omega_{ba} n_a$. And this one is B_{ba} , the same $U \omega_{ba} n_b$. And we can factor the U out. And this is the

wrong calculation, I must say, because we're missing that extra process that was intuitive to Einstein, but to us it's a little less clear-- N_b times U of ω_{ba} .

OK, I can do a one more little thing. I can factor an N_a . And this becomes B_{ab} minus B_{ba} to the minus $\beta \hbar \omega_{ba} U$ of ω_{ba} . OK, I use the ratio of N_a over N_b being thermodynamical. So N_b over N_a was used from point two to get this. And this should be equal to 0.

But this equation can't be satisfied. What do you have here? You should be able to equilibrate at any temperature. On the other hand, what is our intuition about these quantities, B_{ab} and B_{ba} ? They should be temperature independent. These are properties of the geometry of those states and the overlaps of the wave functions. These are atomic physics properties of the levels of the particles. We will calculate them.

And here is the input of how many photons there are, how many atoms there are. And the number of photons certainly depend on the temperature. The number of atoms for equilibrium depend on the temperature. But this is a factor that says, well, how likely is the transition once you have a photon and once you have an atom? And that depends like we did for the ionization, calculated some matrix elements that are totally independent of temperature.

So these numbers are totally independent of temperature. And we're asking this to be 0, which requires this factor to be 0. And this depends on temperature. So you cannot attain equilibrium with this way. So it's impossible to satisfy for all temperatures given that B_{ab} and B_{ba} are constants.

So we're missing a process. This is the process that Einstein thought was intuitive, the process of spontaneous emission. So we add one more process. It's called spontaneous emission.

And it's a process also from b to a . And it's going to have a rate. But it's not going to depend, that rate, on the number of photons, because it's happening independently of the photons. So we don't have this U factor. We do have the N_b because each of the b atoms can spontaneously decay. But we don't have the U factor.

So what do we have? A rate, which is the term by a coefficient that Einstein called it a , that's why the name a and b coefficients of Einstein, a times b . So that's the spontaneous emission rate per atom multiplied by the number of atoms.

So we go back to our equation-- rate of absorption minus rate of stimulated emission minus the rate of spontaneous emission. So I'll write it here. $0 = \dot{N}_b = -A_{21} N_b - B_{21} U \omega_{ba} N_b + B_{12} U \omega_{ba} N_a$.