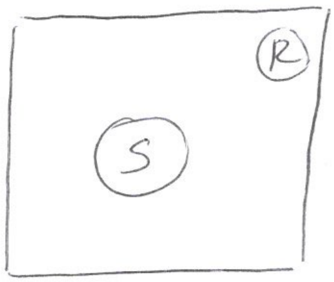
Consider a small volume of ISM inside a huge cloud of ISM. Let's call the small volume S and the huge one R.



S can absorb energy from R and give energy to R, but R is so large that we can consider that the energy remains constant in R

S is a system that can be in two energy states

—— E_a

—— E_b

~~Consider~~ Assume that the energy difference is 1 and that the reservoir has 10 particles and an initial energy $U_0 = 100$ units. In how many ways can the energy be distributed among the 10 particles? E.g.

Particle	State 1	State 2	State 3	...	State p	...	State q
1	100	99	98		10		0
2	0	1	1		10		0
3	0	0	1		10		0
4	0	0	0		10		0
5	0	0	0		10		0
6	0	0	0		10		0
7	0	0	0		10		0
8	0	0	0		10		0
9	0	0	0		10		0
10	0	0	0		10		100

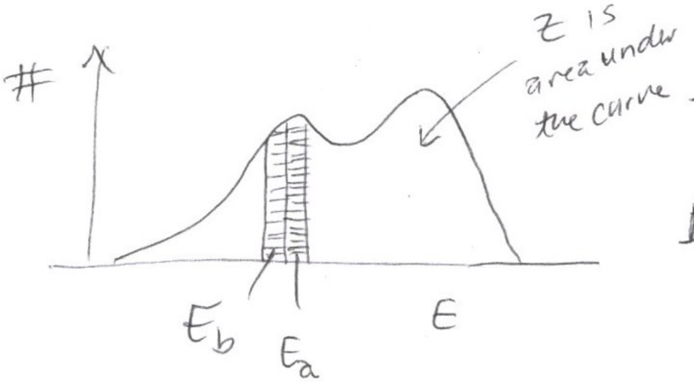
The actual number does not matter, only the fact that there is in principle a number of ways the energy can be arranged. Let's call it $g_R(U_0)$.

If R loses 1 unit of energy to S and $U - E_b = 99$, ~~is the num~~ IS THE NUMBER OF WAYS THE ENERGY CAN BE ARRANGED THE SAME FOR $g_R(U_0)$ and $g_R(U-E_b)$

IS IT GREATER? LOWER? ??

In general, whether it is greater or lower depends on the specifics of the system, but what really matters here is that $g_R(U_0)$ and $g_R(U_0-E_b)$ can be different.

If we want to know whether S is in the energy state A or B, we could measure the energy of R. if there are many energy states, we can't know for sure, but we can get a probability.



$$P(E_b) = g_R(U_0 - E_b)/Z$$

$$P(E_a) = g_R(U_0 - E_a)/Z$$

*WHAT IS THE RATIO OF THE PROBABILITIES?

$$\frac{P(E_b)}{P(E_a)} = \frac{g_R(U_0 - E_b)/\cancel{Z}}{g_R(U_0 - E_a)/\cancel{Z}}$$

The definition of entropy is the natural log of the number of states available to the system, so (times k_B) $S = k_B \ln g$

$$\frac{P(E_b)}{P(E_a)} = \frac{\exp\{\ln[g_R(U_0 - E_b)]\}}{\exp\{\ln[g_R(U_0 - E_a)]\}} = \frac{\exp[S_R(U_0 - E_b)/k_B]}{\exp[S_R(U_0 - E_a)/k_B]}$$

$$= \exp\left[\frac{S_R(U_0 - E_b) - S_R(U_0 - E_a)}{k_B}\right]$$

Let $\Delta S_R \equiv S_R(U_0 - E_b) - S_R(U_0 - E_a)$, then

$$\frac{P(E_b)}{P(E_a)} = \exp\left[\Delta S_R / k_B\right]$$

The ratio of the probabilities is ~~the~~ proportional ~~to the exponent~~ to e^S entropy

Here we can do a Taylor expansion, $f(x) \approx f(a) + f'(a)(x-a) + \frac{f''(a)(x-a)^2}{2!} + \ldots$ about U_0, since E is small.

Let $x = U_0 - E_1$

$a = U_0$

$\cancel{S_R(U_0) \approx S_R(U_0)}$

$$S_R(U_0 - E_b) \approx S_R(U_0) + (U_0 - E_b - U_0)\left.\frac{dS_R}{dU}\right|_{U=U_0}$$

$$+ \frac{1}{2}(U_0 - E_b - U_0)^2 \left.\frac{d^2 S_R}{dU^2}\right|_{U=U_0}$$

$$S_R(U_0 - E_b) \approx S_R(U_0) - E_b \left.\frac{dS_R}{dU}\right|_{U=U_0} + \frac{1}{2} E_b^2 \left.\frac{d^2 S_R}{dU^2}\right|_{U=U_0} - \cdots$$

Similarly,

$$S_R(U_0 - E_a) \approx S_R(U_0) - E_a \left.\frac{dS_R}{dU}\right|_{U=U_0} + \frac{1}{2} E_a^2 \left.\frac{d^2 S_R}{dU^2}\right|_{U=U_0} - \cdots$$

Since E_a and E_b are very small, we can truncate after the first order term. So, to a first approximation,

$$\Delta S_R \approx \cancel{S_R(U_0)} - E_b \left.\frac{dS_R}{dU}\right|_{U=U_0} - \left[\cancel{S_R(U_0)} - E_a \left.\frac{dS_R}{dU}\right|_{U=U_0}\right]$$

$$\Delta S_R \approx \left.\frac{dS_R}{dU}\right|_{U=U_0} \left[-(E_b - E_a)\right]$$

The units of $\cancel{d}\, S_R$ are k_B, J/K

The units of U are J

The units of $\frac{dS_R}{dU}$ are $\frac{J/K}{\cancel{K}J} = \frac{1}{K}$. $\frac{dS_R}{dU}$ is in fact $\frac{1}{T}$

$$\Delta S_R \approx -\frac{(E_b - E_a)}{T}, \text{ so}$$

$$\frac{\rho(E_b)}{\rho(E_a)} = \exp\left[-\frac{(E_b - E_a)}{k_B T}\right] = \frac{\exp[-E_b/k_B T]}{\exp[-E_a/k_B T]}$$

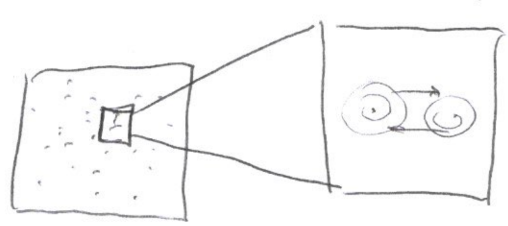
$$\rho(E_a) = \frac{n_a}{g_A}, \quad \rho(E_b) = \frac{n_b}{g_B}$$

$$\frac{\rho(E_a)}{\rho(E_b)} = \frac{n_a/g_a}{n_b/g_b} = \frac{n_a g_b}{n_b g_a} = \frac{\exp[-E_a/k_B T]}{\exp[-E_b/k_B T]}$$

$$n_a/n_b = \frac{g_a \exp[-E_a/k_B T]}{g_b \exp[-E_b/k_B T]}$$

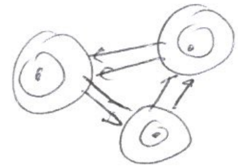
The principle of detailed balance was introduced by Boltzman in 1872 and used it to prove that entropy always increases in a system which initially has low entropy. It states simply that in equilibrium, each process in a system is in equilibrium with its reverse process.

From the outside it looks like nothing happens, but if you zoom in, you can see that the particles of a system are interacting



moving energy back and forth.

The processes should be elemental, detailed balance is based on microscopic reversibility (the laws of physics are the same in $+t$ and $-t$). Cyclical process that conserve energy do not seem to contribute to equilibrium



. Local detailed balance is the basis of non-equilibrium thermodynamics ☆

Einstein used detailed balance with his coefficients

$$B_b^a n_b - B_a^b n_a = A_a^b n_a$$

n_a number density of particles in energy level a

n_b energy level b

Absorption $E_b \to E_a$

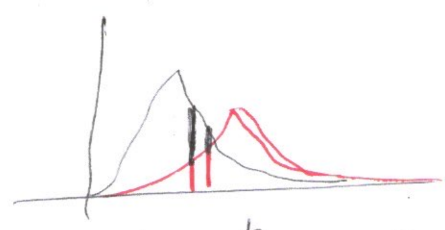
stimulated emission $E_a \to E_b$

spontaneous emission $E_a \to E_b$

$$\rho(\nu_{ab}, T)\left(B_b^a g_b e^{-E_b/k_BT} - B_a^b g_a e^{-E_a/k_BT}\right) = A_a^b g_a e^{-E_a/k_BT} \quad \underline{W3.1.13}$$

Applying the condition that the black-body radiation spectrum is unchanged, multiply times $\rho(\nu, T)$

$$\rho(\nu, T) = \frac{8\pi h\nu^3}{c^3}\left[\frac{1}{e^{h\nu/k_BT} - 1}\right]$$



W3.1.13 should hold for all temperatures, but B_a^b, B_b^a, A_a^b are ~~aa~~ atomic energy levels and hence temperature-independent. This leads to:

This leads to:

$$B_b^a g_b = B_a^b g_a \quad \text{and} \quad A_a^b = \left(\frac{8\pi h\nu_{ab}^3}{c^3}\right) B_a^b$$

Since

emission lineshape

$$K(\nu) = h\nu\,\phi(\nu)\left(B_b^a n_b - B_a^b n_a\right)/c$$

number of particles in state b

transition rate from b to a $E_b < E_a$

fraction of photon energy absorved by the medium per distance traveled

$$K(\nu) = h\nu\phi(\nu)\left(B_a^b n_b - B_a^b n_a\right)/c = h\nu\phi(\nu)\left(B_b^a n_b - B_b^a n_a\right)/c$$

$$= \cancel{h\nu\phi(\nu)\, B_b^a\left[\frac{g_b e^{-E_b/k_BT}}{g_b e^{-E_a/k_BT}} n_a - n_a\right.}$$

$$K(\nu) = h\nu\phi(\nu)\left[n_b - \frac{g_a e^{-E_a/k_BT}}{g_b e^{-E_b/k_BT}} n_b\right] B_b^a/c$$

$$K(\nu) = h\nu\phi(\nu)\left[1 - \frac{g_a e^{-E_a/k_BT}}{g_b e^{-E_b/k_BT}}\right] B_b^a n_b/c \implies \text{algebra}$$

$$1 - g$$

$$K(\nu) = h\nu\phi(\nu)\left[1 - \frac{g_a \cancel{e^{-E_a/k_BT}}}{g_b\left(\frac{\cancel{e^{-E_a/k_BT}}}{n_a/n_b}\right)}\right] B_b^a n_b/c$$

$$K(\nu) = h\nu\phi(\nu)\left[1 - \frac{g_a}{\frac{1}{\frac{g_b/1}{n_a/n_b}}}\right] B_b^a n_b/c = h\nu\phi(\nu)\left[1 - \frac{g_a}{\frac{1}{\frac{g_b n_b}{n_a}}}\right] B_b^a n_b/c$$

$$K(\nu) = h\nu\phi(\nu)\left[1 - \frac{n_a/g_a}{n_b/g_b}\right] B_b^a n_b / c$$

Similarly, with $J(\nu) = h\nu\,\phi(\nu)\, A_a^b n_a$, we end up

$$\frac{J(\nu)}{K(\nu)} = \left(\frac{8\pi h \nu_{ab}^3}{c^2}\right)\left[\frac{n_b/g_b}{n_a/g_a} - 1\right]^{-1}$$

Energy diff

$$\frac{J(\nu)}{K(\nu)} = \left(\frac{8\pi h \nu_{ab}^3}{c^2}\right)\left[\exp\left(\frac{h\nu_{ab}}{k_B T}\right) - 1\right]^{-1}$$

Remember

$$\ell(\nu,s) = e^{-\tau}\ell(\nu,s_1) + \frac{J(\nu)}{4\pi c K(\nu)}\left[1 - e^{-\tau(\nu,s)}\right] \qquad \underline{W3.1.6}$$

with $\tau(\nu,s) \equiv \int_{s_1}^{s} K(\nu,s')\,ds'$

if we consider s_1 to be the far end of a cloud, then $\ell(\nu,s_1) = 0$ and

$$\ell(\nu,s) = \frac{J(\nu)}{4\pi c K(\nu)}\left[1 - e^{-\tau(\nu,s)}\right] = \frac{\rho(\nu_{ab},T)}{4\pi}\left[1 - e^{-\tau(\nu,s)}\right]$$

$$\tau(\nu,s) = h\nu\phi(\nu) B_b^a \left[1 - \exp\left(-\frac{h\nu_{ab}}{k_B T}\right)\right]\frac{N_b(s)}{c}$$ where

$$N_b(s) = \int_{s_1}^{s} n_b(s')\,ds \leftarrow \text{column density}$$