The Gibbs state

In most of this course, we will be interested in systems which are in thermal equilibrium. Consider an arbitrary physical system, described by a Hamiltonian H with eigenstuff

$$H|n\rangle = E_n |n\rangle \tag{1}$$

this can be anything, from a single electron to 10^{23} particles. If this system is in thermal equilibrium, then the probability of finding it in state $|n\rangle$ will be given by

$$\boxed{P_n = \frac{e^{-\beta E_n}}{Z}} \tag{2}$$

which is called the Gibbs state. Here

$$\beta = \frac{1}{k_B T} = \frac{1}{T} \qquad (k_B = 1) \tag{3}$$

where T is the temperature and k_B is Boltzmann's constant, which I set to $k_B = 1$. Moreover, the quantity Z in Eq (2) is a normalization constant called the partition function

$$\boxed{Z = \sum_n e^{-\beta E_n}} \tag{4}$$

Eq (2) is the foundation for all of equilibrium statistical mechanics. So now there are two things left for us to do. We can either try to understand why Eq (2) is true (maybe even try to derive it) or we can simply apply it to a bunch of problems and see what comes out. We shall do both.

Once we have the probabilities (2), the next big thing is to compute the expectation value of observables. Given any observable A, its expectation value in the Gibbs state will be given by

$$\boxed{\langle A \rangle = \sum_n \langle n | A | n \rangle P_n} \tag{5}$$

You can see that is a type of double expectation value: it is the expectation value $\langle n|A|n\rangle$ in each energy eigenstate, weighted by the Gibbs probabilities P_n.

The most important observable is the Hamiltonian. The expectation value $\langle H \rangle$ receives a special name, the <u>internal energy</u>, and a special symbol U. Since $\langle n|H|n\rangle = E_n$, we thus get

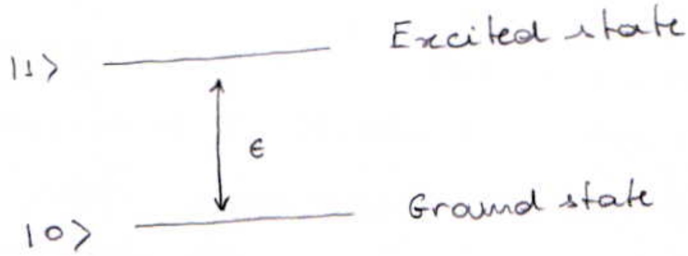
$$\boxed{U = \langle H \rangle = \sum_n E_n P_n} \tag{6}$$

Example: qubit (2-level system)

As our first example, we consider a system that has only two energy levels, which we label as $|0\rangle$ and $|1\rangle$. That is,

$$H|0\rangle = E_0 |0\rangle$$
$$H|1\rangle = E_1 |1\rangle \qquad (7)$$

Since energy is defined only up to a constant, we may, without loss of generality, set $E_0 = 0$ and $E_1 = \epsilon$. Then $|0\rangle$ is the ground state, $|1\rangle$ is the excited state and ϵ is the energy gap between them



In this case the partition function (4) becomes

$$\boxed{Z = e^{-\beta E_0} + e^{-\beta E_1} = 1 + e^{-\beta \epsilon}} \qquad (8)$$

whereas the Gibbs probabilities become

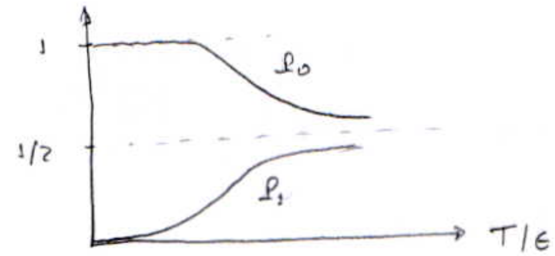
$$P_0 = \frac{1}{1 + e^{-\beta\epsilon}} \qquad (9)$$

$$P_1 = \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} = \frac{1}{e^{\beta\epsilon} + 1} \qquad (10)$$

The probabilities only depend on the quantity

$$\beta\epsilon = \frac{\epsilon}{T}$$

this makes intuitive sense: the probabilities of occupation depend only on the ratio of the energy gap to the thermal energy. In terms of T/ϵ the probabilities P_0 and P_1 look like this



The probability of being found in the ground state (GS) is always larger. As $T \to 0$ we get $P_0 = 1$ and $P_1 = 0$. So at zero temperature the system "settles down" in $|0\rangle$. Conversely, if $T \to \infty$, then both P_0 and P_1 tend to $1/2$. In this case you are equally likely to find the system in either $|0\rangle$ or $|1\rangle$.

The prob. P_1 in Eq (10) represents the prob. of finding the system in the excited states. For reasons that will become clear later on, it is called the Fermi - Dirac distribution. The internal energy, Eq (6), becomes in this case

$$\boxed{U = E_0 P_0 + E_1 P_1 = \epsilon P_1} \tag{11}$$

Thus, the plot of P_1 in the figure above is also a plot of U. We therefore see that energy increases monotonically with temperature, which makes sense

Example: the harmonic oscillator

As our second example, we consider the harmonic oscillator, with energy eigenvalues

$$E_n = \hbar\omega(n+1/2) \qquad n = 0, 1, 2, \dots \tag{12}$$

In this course I also set $\hbar = 1$ so, neglecting the irrelevant $\hbar\omega/2$ as well, we can simply write

$$E_n = \omega n \qquad n = 0, 1, 2, \dots \tag{13}$$

the partition function becomes

$$Z = \sum_{n=0}^{\infty} e^{-\beta\omega n}$$

If we define $x = e^{-\beta\omega}$ then we identify here a geometric series

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \tag{14}$$

Moreover, in our case the series is always convergent since $e^{-\beta\omega} < 1$ (because both β and ω must be positive). Hence

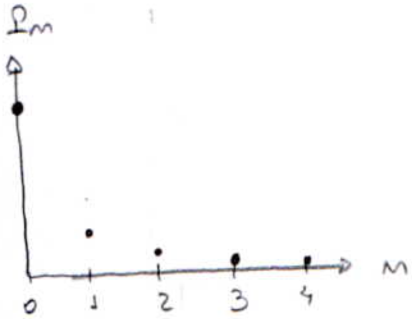
$$\boxed{Z = \frac{1}{1 - e^{-\beta\omega}}} \tag{15}$$

The Gibbs probabilities p_n in (2) then become

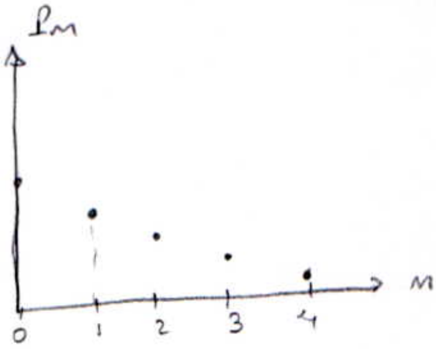
$$\boxed{p_n = (1 - e^{-\beta\omega})\, e^{-\beta\omega n}} \tag{16}$$

In probability theory this is known as the geometric distribution.

They look something like this:



$\frac{T}{\omega}$ small

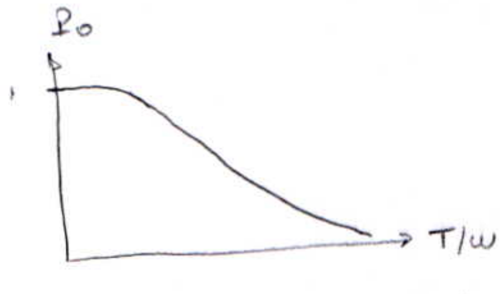


$\frac{T}{\omega}$ large

It always goes down with n: lower energy states are always more likely. For T/ω large it decreases slowly, whereas for T/ω small it is highly concentrated around $|0\rangle$ and goes down fast with $|n\rangle$. Indeed, from (16) we see that the probability of finding the system in the GS is

$$p_0 = 1 - e^{-\beta\omega} \tag{17}$$

which looks like this



Thus, as $T \to 0$ we get $p_0 = 1$: the system is found with certainty in the GS. For $T \to \infty$, on the other hand, $p_0 \to 0$ since in this case the probabilities become diluted over many states.

The average energy (6) in this case becomes

$$U = \sum_{n} \omega n P_n \tag{18}$$

It is convenient to get rid of the ω in front and simply speak of the average occupation number

$$\langle n \rangle = \sum_{n=0}^{\infty} n P_n = (1 - e^{-\beta\omega}) \sum_{n=0}^{\infty} n e^{-\beta\omega n} \tag{19}$$

This sum can be computed using the following neat trick. Differentiate the geometric series (14) with respect to x:

$$\sum_{n=0}^{\infty} n x^{n-1} = \frac{1}{(1-x)^2}$$

Now multiply by x on both sides to get

$$\sum_{n=0}^{\infty} n x^{n} = \frac{x}{(1-x)^2} \tag{20}$$

Thus (19) becomes

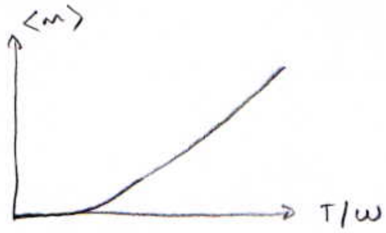
$$\langle n \rangle = (1 - e^{-\beta\omega}) \frac{e^{-\beta\omega}}{(1-e^{-\beta\omega})^2} = \frac{e^{-\beta\omega}}{1 - e^{-\beta\omega}}$$

or, what is more convenient,

$$\boxed{\langle n \rangle = \frac{1}{e^{\beta\omega} - 1}} \tag{21}$$

Again for reasons that will become clear later on, this is called the Bose-Einstein distribution. It looks similar to (10), except for the minus sign.

The function $\langle n \rangle$ looks like this



For $T \to 0$ we get $\langle n \rangle = 0$ (no occupation). Then it curves up and for large T it becomes linear.

It is also sometimes convenient to note that we can write (21) as

$$\boxed{\langle n \rangle + 1/2 = \frac{1}{2} \coth\left(\frac{\beta \omega}{2}\right)} \tag{22}$$

For small x

$$\coth(x) \simeq \frac{1}{x} \tag{23}$$

so we get, for large T/ω,

$$\langle n \rangle + 1/2 \simeq \frac{T}{\omega} \tag{24}$$

If we reinstitute the $1/2$ that I threw away in the energy (12), we then get

$$\boxed{U = \frac{\omega}{2} \coth\left(\frac{\beta \omega}{2}\right)} \tag{25}$$

For large T we get $U \simeq T$.

Why the Gibbs state?

Now I want to argue with you as to why the Gibbs formula (2) makes sense. I will not try to be rigorous, but simply appeal to our intuition.

I will start by making one fundamental postulate, which is present in all theoretical formulations of statistical mechanics.

$$\boxed{\text{Postulate of equal a priori probabilities: quantum states with the same energy are equally likely}} \tag{26}$$

This puts energy on a pedestal: it says that as a consequence of the complicated microscopic interactions in nature, when a system is in equilibrium, the energy is the only thing which can tell states apart.

This postulate means that the probabilities P_n of a given state $|n\rangle$ must be a function only of its energy E_n:

$$P_n = f(E_n) \tag{27}$$

where $f(x)$ is some unknown function. Now I want to convince you that this function must be an exponential.

To do that, let's imagine just for now that we actually have two system, A and B, both in equilibrium. And we assume that they do not interact at all so the total energy will be

$$E_n^A + E_m^B$$