

Gibbs formalism for quantum systems

Gabriel T. Landi

Summary of main formulas

classical	Quantum
$P(y) = \frac{e^{-\beta H(y)}}{Z}$	$P_m = \frac{e^{-\beta E_m}}{Z}$
$Z = \int Dy e^{-\beta H(y)}$	$Z = \sum_m e^{-\beta E_m}$
$U = \langle H \rangle = \int H(y) P(y) Dy$	$U = \langle E_m \rangle = \sum_m E_m P_m$
$C = \frac{\partial U}{\partial T}$ $F = -k_B T \ln Z$	

References :

- Salinas, chapter 5

Quantum systems

Now we will extend the Gibbs formalism to include quantum systems. The big difference is that in quantum systems the energies take on a discrete set of values

$$\text{Energy} = E_1 \text{ or } E_2 \text{ or } E_3 \text{ or } E_4 \text{ or } \dots$$

We usually write these energies as E_m , where m is called a quantum number.

The microstate of a quantum system is specified by a set of quantum numbers.

Ex: a spin-1/2 system has quantum number $S = +\frac{1}{2}$ or $\sigma = -\frac{1}{2}$. The energy in the presence of a magnetic field B is $E_\sigma = -\mu_B B S$, where μ_B is a constant

Ex: A quantum harmonic oscillator has a quantum number

$$m = 0, 1, 2, 3, \dots$$

with energy levels

$$E_m = \hbar\omega (m + 1/2)$$

(11)

The extension of the Gibbs formalism to quantum systems is straightforward. But now, instead of integrating over a continuous microstate y , we sum over discrete microstates

m .

$$P_m = e^{-\beta E_m} \quad z = \sum_m e^{-\beta E_m} \quad (4)$$

Please note that " m " here means a generic description of the quantum numbers. So you should always sum over all quantum numbers. For instance, in the case of the Hydrogen atom we would have

$$z = \sum_{n, l, m, s} e^{-\beta E_m} \quad (5)$$

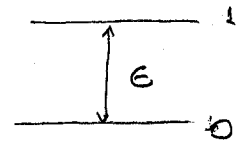
Even though the energy depends only on n , we sum over all states [remember: $z = z_0$ and $z_0 = \sum_{\text{states}} e^{-\beta E}$].

Example: two-state system

Suppose a system has only two states.

ground state: 0: $E_0 = 0$

excited state: 1: $E_1 = \epsilon$



(6)

The zero of energy is arbitrary so we set it in order to have state 0 with $E_0 = 0$.

The partition function will be

$$z = \sum_{m=0,1} e^{-\beta E_m} = e^{-\beta E_0} + e^{-\beta E_1}$$

$$\therefore z = 1 + e^{-\beta \epsilon}$$

(7)

The probabilities are then $P_m = e^{-\beta E_m} / z$, or

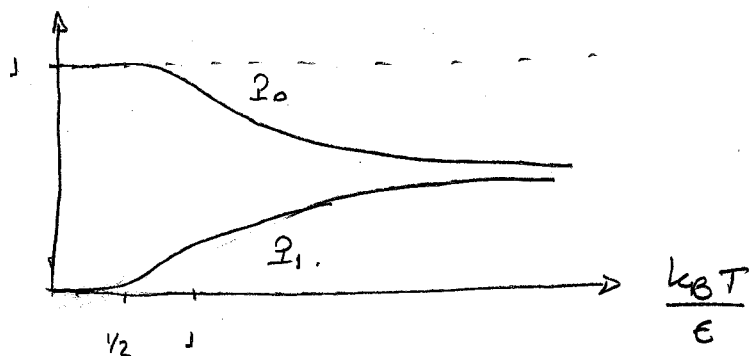
$$P_0 = \frac{1}{1 + e^{-\beta \epsilon}}$$

$$P_1 = \frac{e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} = \frac{1}{e^{\beta \epsilon} + 1}$$

(8)

P_1 is known as the Fermi-Dirac distribution. It gives you the probability of finding the system in the excited state.

these probabilities look like this:



From this plot we learn a really valuable lesson:

when $T = 0$ the system always tends to the ground state

(98)

You should remember this for the rest of your life! The prob. P_0 always tends to 1 when $T \rightarrow 0$. This is why, when we discuss the configuration of electrons in atoms we put them in the lowest energy states. Because at low temperatures that is predominantly where they will stay.

In the opposite limit, as $T \rightarrow \infty$, P_0 and P_1 both tend to $1/2$. At infinite temperatures all states become equally likely.

Note also that we always have $P_0 > P_1$. This is something we used already when deriving the Gibbs formula. It is related to the thermodynamic stability of the system.

← Coffee stains

The average energy is

$$U = \langle E_m \rangle = \sum_m E_m P_m \quad (10)$$

In our case we get

$$U = E_0 P_0 + E_1 P_1$$

or

$$U = \frac{\epsilon}{e^{\beta\epsilon} + 1} \quad (11)$$

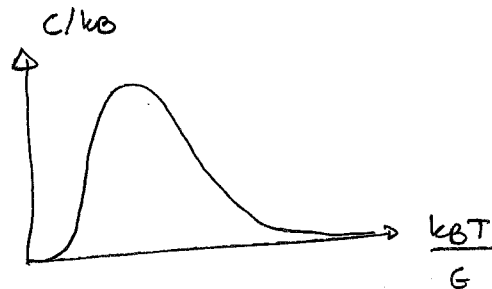
The heat capacity is

$$C = \frac{\partial U}{\partial T} = \frac{-\epsilon}{(e^{\beta\epsilon} + 1)^2} \frac{\partial}{\partial T} (e^{\epsilon/k_B T})$$

$$C = \frac{\epsilon^2}{k_B T^2} \frac{e^{\beta\epsilon}}{(e^{\beta\epsilon} + 1)^2} \quad (12)$$

The graph of U/ϵ vs $k_B T/\epsilon$ looks just like the graph of P_1 .

As for C , we have



The free energy is

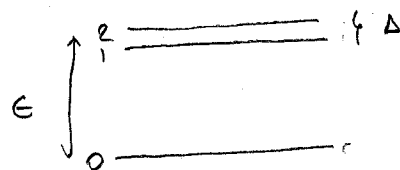
$$F = -k_B T \ln Z = -k_B T \ln (1 + e^{-\epsilon/k_B T}) \quad (13)$$

Example: a 3-state system and the role of degeneracy

Consider now a system with the following level structure

$$\begin{aligned} \text{ground state } 0 & : E_0 = 0 \\ \text{excited state } 1 & : E_1 = \epsilon + \Delta \\ \text{excited state } 2 & : E_2 = \epsilon - \Delta \end{aligned} \quad (14)$$

this looks like this:



when $\Delta = 0$ states 1 and 2 become degenerate.

the partition function is

$$\begin{aligned} z &= \sum_m e^{-\beta E_m} = 1 + e^{-\beta(\epsilon + \Delta)} + e^{-\beta(\epsilon - \Delta)} \\ &= 1 + e^{-\beta\epsilon} \underbrace{(e^{-\beta\Delta} + e^{\beta\Delta})}_{2 \cosh \beta\Delta} \end{aligned}$$

$$\therefore z = 1 + 2 e^{-\beta\epsilon} \cosh(\beta\Delta) \quad (15)$$

Note how z is always a sum over states and never a sum over energies. Even if $\Delta = 0$ we still have a sum of 3 terms (not 2). In this case we would get

$$\Delta = 0: \quad z = 1 + 2 e^{-\beta\epsilon} \quad (16)$$

which is different from (7). You see, when $\Delta \rightarrow 0$ we do not obtain a 2-state system. We continue to have a 3 state system, but with 2 degenerate levels.

Example: The quantum harmonic oscillator (QHO)

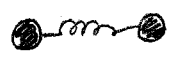
In your quantum mechanics course you will learn that the energy levels of a quantum harmonic oscillator are

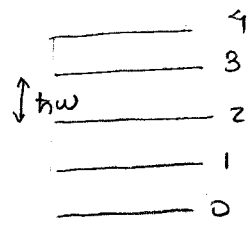
$$E_m = \hbar\omega(m + 1/2), \quad m = 0, 1, 2, 3, \dots \quad (17)$$

The ground state (state of smallest energy) is that with $m=0$:

$$E_0 = \hbar\omega/2 \quad (18)$$

This is called the zero-point fluctuations. The excited states are all equally spaced ($\Delta E = \hbar\omega$), which is a signature of the harmonic oscillator.

When we think about the QHO, I want you to have two models in mind. The first is the vibration of a diatomic molecule (like O_2). To a very good approximation, these vibrations are harmonic.  Then m represents the number of quanta of vibration a molecule has.



The other model to have in mind are photons. You may remember the formula that the energy of a single photon is $E = h\nu$. But $h\nu = (2\pi\hbar)(\omega/2\pi) = \hbar\omega$. Thus, the energy of m photons will be $E_m = m\hbar\omega$. We see that, apart from the factor of $\hbar\omega/2$, which is just a constant energy shift, this is the same as Eq. (17).

The partition function is

$$z = \sum_{m=0}^{\infty} e^{-\beta \hbar \omega (m+1/2)} = e^{-\beta \hbar \omega / 2} \sum_{m=0}^{\infty} e^{-\beta \hbar \omega m} = e^{-\beta \hbar \omega / 2} \sum_{m=0}^{\infty} x^m$$

$x = e^{-\beta \hbar \omega}$

This is a geometric series

$$\sum_{m=0}^{\infty} x^m = \frac{1}{1-x} \quad (19)$$

In our case the series always converges because $\beta \hbar \omega > 0$ (we would be in trouble if negative temperatures were allowed).

We then get

$$z = \frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}} \quad (20)$$

The Gibbs probabilities are then

$$P_m = \frac{e^{-\beta E_m}}{z} = \frac{(1 - e^{-\beta \hbar \omega})}{e^{-\beta \hbar \omega / 2}} e^{-\beta \hbar \omega (m+1/2)}$$

Notice how the factor of $\beta \hbar \omega / 2$ will cancel out. This is reasonable. After all, a constant shift in all the energy levels should not affect the probabilities. We then get

$$P_m = (1 - e^{-\beta \hbar \omega}) e^{-\beta \hbar \omega m} \quad (21)$$

This is the Geometric distribution $P_m = (1-p)^m p$, with $p = 1 - e^{-\beta \hbar \omega}$

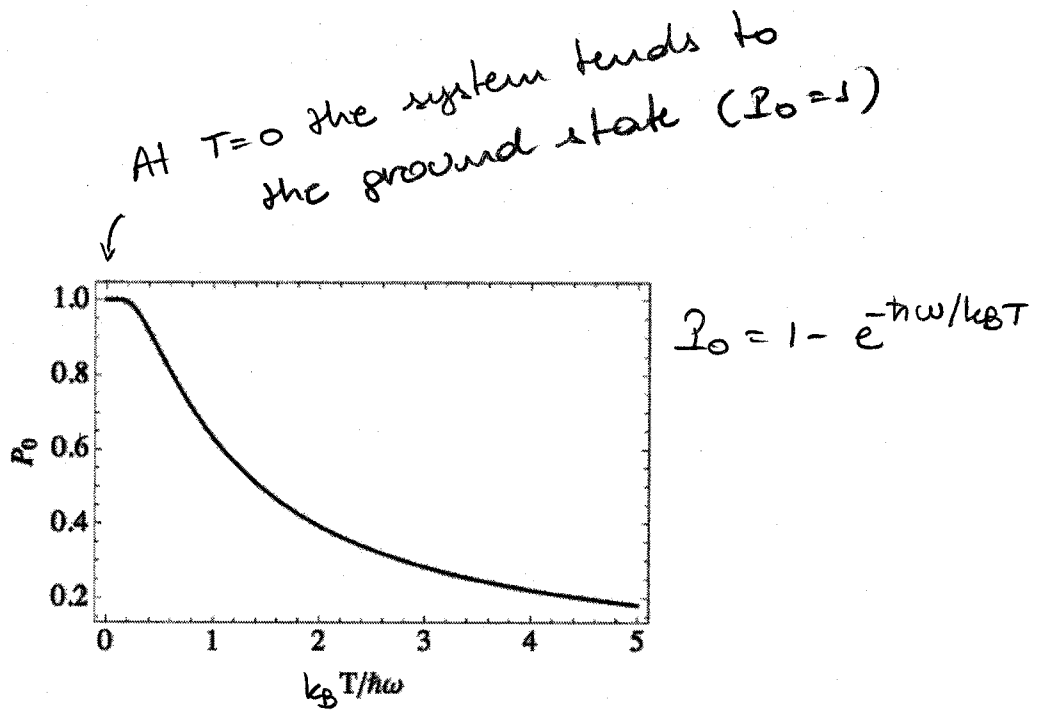


Figure 1.8: Probability P_0 of finding the harmonic oscillator in the ground state, computed from Eq. (38) as a function of the dimensionless temperature $T/\hbar\omega$. (38)

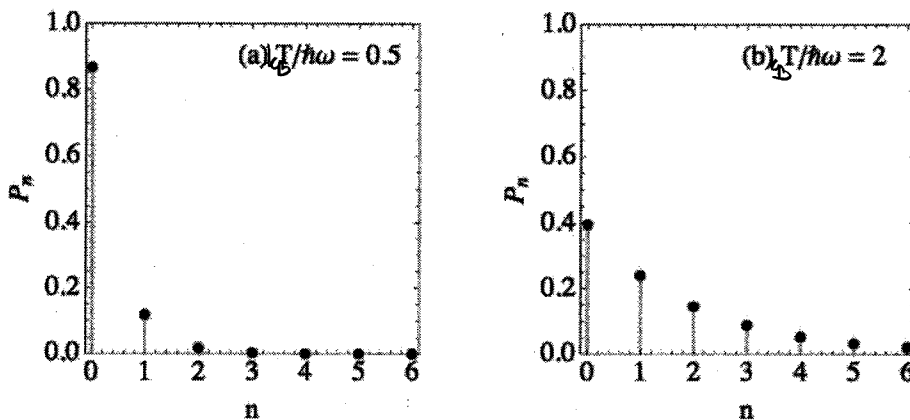


Figure 1.9: Probabilities P_n for the quantum harmonic oscillator computed from Eq. (38) for two different values of $T/\hbar\omega$, as shown in each image. (38)

↑
Note that $P_0 > P_1 > P_2 > \dots$

↑
This is thermodynamic stability.

The most important quantity to compute in this problem is the average number of quanta, $\langle n \rangle$. Using (21) we find

$$\langle n \rangle = \sum_{m=0}^{\infty} m P_m = (1 - e^{-\beta \hbar \omega}) \sum_{m=0}^{\infty} m x^m$$

Now:

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

Thus

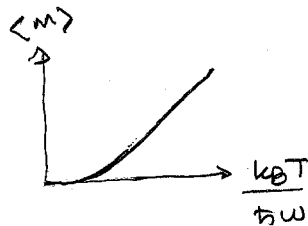
$$\langle n \rangle = (1 - e^{-\beta \hbar \omega}) \frac{e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2} = \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}$$

It is more convenient to write this as

$$\langle n \rangle = \frac{1}{e^{\beta \hbar \omega} - 1}$$

(22)

This is known as the Bose-Einstein distribution (compare with Eq (8)). It looks like this



As expected, it tends to zero when $T=0$

The internal energy can be found from linearity:

$$U = \langle E_m \rangle = \hbar\omega (\langle m \rangle + 1/2) = \hbar\omega \left[\frac{1}{e^{\beta\hbar\omega} - 1} + 1/2 \right]$$

or we can find it from Z in Eq (20)

$$\begin{aligned} U &= -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta} \left\{ -\frac{\beta\hbar\omega}{2} - \ln(1 - e^{-\beta\hbar\omega}) \right\} \\ &= \frac{\hbar\omega}{2} + \frac{\partial}{\partial \beta} \ln(1 - e^{-\beta\hbar\omega}) \\ &= \frac{\hbar\omega}{2} + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \end{aligned}$$

There is also a neat way to write this:

$$U = \frac{\hbar\omega}{2} \left\{ \frac{2 + e^{\beta\hbar\omega} - 1}{e^{\beta\hbar\omega} - 1} \right\} = \frac{\hbar\omega}{2} \left[\frac{e^{\beta\hbar\omega} + 1}{e^{\beta\hbar\omega} - 1} \right] = \frac{\hbar\omega}{2} \frac{e^{\beta\hbar\omega/2}}{e^{\beta\hbar\omega/2}} \left[\frac{e^{\beta\hbar\omega/2} + e^{-\beta\hbar\omega/2}}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}} \right]$$

The function inside the brackets is

$$\frac{e^x + e^{-x}}{e^x - e^{-x}} = \coth(x)$$

thus, we conclude that

$$U = \hbar\omega (\langle m \rangle + 1/2) = \frac{\hbar\omega}{2} \coth\left(\frac{\beta\hbar\omega}{2}\right) \quad (23)$$

This looks something like:



At $T=0$ we see that U tends to the ground state, $U = E_0 = \frac{\hbar\omega}{2}$.

Let's see what happens in the opposite limit, at high temperatures.

In this case $\frac{\hbar\omega}{k_B T} \ll 1$ so we may expand $\coth(x)$. It's first

Taylor series coefficient is

$$\coth(x) \approx \frac{1}{x}$$

Thus, Eq (23) will give

$$U \approx \frac{\hbar\omega}{2} \frac{2 k_B T}{\hbar\omega} = k_B T \quad (24)$$

This is the same as the result of a classical harmonic oscillator. We therefore reach the following conclusion, which turns out to be valid quite generally

At high T quantum results approach their classical counterparts

Or, putting it differently,

Quantumness is washed away at high T

Specific heat and the Einstein model

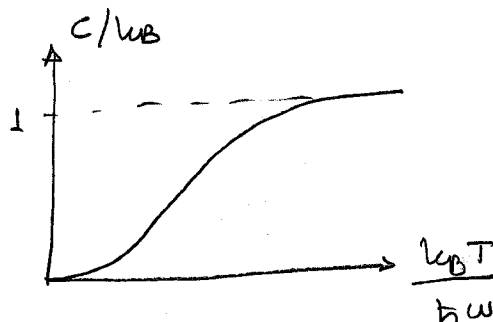
The heat capacity will be, from (23)

$$c = \frac{\partial U}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial U}{\partial \beta} = -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta} \left[\frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right]$$
$$= -\frac{\hbar \omega}{k_B T^2} \frac{-\hbar \omega e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}$$

Thus

$$c = k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} \quad (25)$$

this looks like:



At high temperatures it tends to the classical result, $c = k_B$.
But at low temperatures it tends to zero.

Recall from our previous discussion that one could model a solid as a collection of $3N$ independent harmonic oscillators. For classical oscillators we then found a heat capacity of

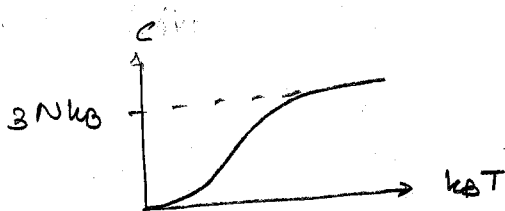
$$c = 3Nk_B \quad (26)$$

which is the Dulong and Petit law.

This law only holds for high temperatures. At low temperatures Einstein proposed to use instead the quantum result (25). That is, we should model the heat capacity of a solid as

$$c = 3Nk_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} \quad (27)$$

The only free parameter is ω , which depends on the material in question. This is called the Einstein model.



It reproduces the law of Dulong and Petit at high temperatures.

This model is a big improvement. But it has one unsatisfactory property: at low T it predicts an exponential dependence of c on T . Experimentally, it is found instead that $c \sim T^3$. Later on we will study the Debye model which corrects this deficiency.

Markov chain for a quantum harmonic oscillator

If our QHO is a diatomic molecule, then the heat bath may be the electromagnetic field. The molecule may sometimes absorb a photon and jump from $n \rightarrow n+1$. Or it may sometimes emit a photon and go down a level, $n \rightarrow n-1$. Thus, when the molecule is in contact with the field, its quantum state will undergo a Markov process, jumping around from one state to another.

Of course, this is a process of continuous time, but we may approximate it as a series of discrete time steps. Since the only allowed transitions are between neighboring states, the Markov chain will look like

$$P_n(t+1) = Q_{n,n+1} P_{n+1}(t) + Q_{n,n-1} P_{n-1}(t) + Q_{n,n} P_n(t) \quad (28)$$

↓
Emission
of a
photon

↓
Absorption
of a
photon

↓
Nothing
happens

It can be shown from quantum mechanics that

$$Q_{n,n+1} = \gamma \frac{e^{\beta \hbar \omega}}{e^{\beta \hbar \omega} - 1} (n+1) \quad (29)$$

$$Q_{n,n-1} = \gamma \frac{n}{e^{\beta \hbar \omega} - 1} \quad (30)$$

where γ is a constant which defines the time scale of the problem,

Let's try to understand these results. First, note that the emission probability $\mathcal{A}_{m,m+1}$ depends on $(m+1)$. So the farther up you are in the energy ladder, the higher is the prob. of emitting a photon.

Let us look also at the limit $T \rightarrow 0$. It is convenient to write

$$\frac{1}{e^{\beta \hbar \omega} - 1} = N = \langle n \rangle \quad (31)$$

I write " $\langle n \rangle$ " because this is not the actual $\langle n \rangle$ of the molecule. It is the $\langle n \rangle$ the molecule would have in thermal equilibrium.

Note also that

$$N+1 = \frac{1}{e^{\beta \hbar \omega} - 1} + 1 = \frac{1 + e^{\beta \hbar \omega} - 1}{e^{\beta \hbar \omega} - 1} = \frac{e^{\beta \hbar \omega}}{e^{\beta \hbar \omega} - 1} \quad (32)$$

Thus we see that (29) and (30) may be written as

$$\mathcal{A}_{m,m+1} = \gamma (N+1) (m+1) \quad \mathcal{A}_{m,m-1} = \gamma N m \quad (33)$$

When $T \rightarrow 0$ we already saw that $N=0$. So we obtain

$$T=0: \quad \mathcal{A}_{m,m+1} = \gamma (m+1) \quad \mathcal{A}_{m,m-1} = 0 \quad (34)$$

when $T=0$ the molecule does not absorb any photons. It just emits them. So as time passes it will emit a bunch of photons and eventually settle down at the ground state

Finally, let us verify that this chain satisfies detailed balance:

$$\boxed{Q_{m,m+1} P_{m+1}^{eq} = Q_{m+1,m} P_m^{eq}} \quad (35)$$

where

$$P_m^{eq} = (1 - e^{-\beta h \omega}) e^{-\beta h \omega m}$$

From (30) we have

$$Q_{m,m-1} = \frac{\mu}{e^{\beta h \omega} - 1} m \rightsquigarrow Q_{m+1,m} = \frac{\mu}{e^{\beta h \omega} - 1} (m+1)$$

Thus

$$\frac{Q_{m,m+1}}{Q_{m+1,m}} = \frac{\mu \frac{e^{\beta h \omega}}{e^{\beta h \omega} - 1} (m+1)}{\frac{\mu}{e^{\beta h \omega} - 1} (m+1)} = e^{\beta h \omega}$$

On the other hand

$$\frac{P_m^{eq}}{P_{m+1}^{eq}} = \frac{(1 - e^{-\beta h \omega}) e^{-\beta h \omega m}}{(1 - e^{-\beta h \omega}) e^{-\beta h \omega (m+1)}} = e^{\beta h \omega}$$

Thus, Eq (35) indeed is correct.

Detailed balance is a very 'physical' property. Most physical systems satisfy it.

Spin 1/2 paramagnetism

A particle such as the electron has an intrinsic property called spin, which has two allowed states. We call these states "up" and "down" and we usually write them as

$$\begin{array}{l} \text{up: } \sigma = +1 \text{ or } S = +1/2 \text{ or } \uparrow \\ \text{down: } \sigma = -1 \text{ or } S = -1/2 \text{ or } \downarrow \end{array} \quad (36)$$

I prefer the variable σ because it does not have the factor of $1/2$.

Spins interact with magnetic fields. The energy of interaction is

$$E_{\sigma} = -\mu_B B \sigma \quad (37)$$

where μ_B is a constant called the Bohr magneton, which has the value

$$\begin{aligned} \mu_B &= \frac{e\hbar}{2me} = 5.788 \times 10^{-5} \text{ eV/T} \\ &= 9.274 \times 10^{-24} \text{ J/T} \end{aligned} \quad (38)$$

We therefore have two allowed states

$$\begin{array}{l} \sigma = +1: \quad E_+ = -\mu_B B \\ \sigma = -1: \quad E_- = \mu_B B \end{array} \quad (39)$$

If we assume that $B > 0$ then the ground state (state with the smallest energy) will be $\sigma = +1$. We therefore see that B tends to align the spin in its same direction. But when $T \neq 0$ there will be a certain probability to find the spin at $\sigma = -1$.

By the way, if you prefer you can use the field H instead

$$B = \mu_0 H \quad \mu_0 = 4\pi \times 10^{-7} \text{ Tm/A} \quad (40)$$

In any case, we usually write (37) as

$$E_\sigma = -h\sigma, \quad h = \mu_B B \quad (41)$$

The partition function will be

$$Z = \sum_{\sigma=\pm 1} e^{-\beta E_\sigma} = e^{\beta h} + e^{-\beta h} = 2 \cosh(\beta h) \quad (42)$$

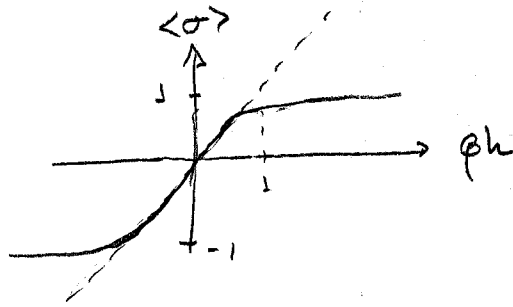
The magnetization will then be

$$\begin{aligned} \langle \sigma \rangle &= \sum_{\sigma} \sigma \mathcal{P}_\sigma = \frac{(+1) e^{\beta h(+1)} + (-1) e^{\beta h(-1)}}{2 \cosh(\beta h)} \\ &= \frac{e^{\beta h} - e^{-\beta h}}{2 \cosh(\beta h)} = \frac{2 \sinh(\beta h)}{2 \cosh(\beta h)} \end{aligned}$$

or

$$\langle \sigma \rangle = \tanh(\beta h) \quad (43)$$

This result looks like this



When $h \rightarrow \infty$ or $T \rightarrow 0$ we see that $\langle \sigma \rangle$ tends to ± 1 , this is the completely magnetized state.

But now let us look at this more carefully. Writing (43) with all physical quantities, we get

$$\langle \sigma \rangle = \tanh \left(\frac{\mu_B B}{k_B T} \right)$$

(44)

But we have

$$\frac{\mu_B}{k_B} = \frac{9.274 \times 10^{-24} \text{ J/T}}{1.38 \times 10^{-23} \text{ J/K}} \approx 0.672 \text{ T/K}$$

When $\mu_B B / k_B T \approx 1$ we begin to observe a deviation of $\tanh(x)$ from a straight line. If $T = 300 \text{ K}$ this means we would need a field of $B \sim 100 \text{ T}$. That is huge! In the lab we usually struggle to get to 10 T.

Thus, we conclude that at room temperatures $\frac{\mu_B B}{k_B T} \ll 1$. We may then expand

$$\tanh(x) \approx x$$

(45)

As a result, we get

$$\langle \sigma \rangle \approx \frac{\mu_B B}{k_B T} \quad (46)$$

This is so common that most people associate the word "paramagnetism" with "magnetization is linear in B". To observe any deviation from a straight line, we need to go to very low temperatures. For instance, if $T = 1$ K, you will already see an effect with fields of the order of $1/2$ T.

The magnetization that is actually measured experimentally is $\mu_B \langle \sigma \rangle$. If we have N independent spins, then the total magnetization will be

$$M = N \mu_B \langle \sigma \rangle \approx \frac{N \mu_B^2 B}{k_B T} \quad (47)$$

The susceptibility is defined as

$$\chi = \frac{\partial M}{\partial B} \quad (48)$$

thus we see that

$$\chi = \frac{N \mu_B^2}{k_B T} = \frac{C}{T} \quad (49)$$

The constant $C = N \mu_B^2 / k_B$ is called the Curie constant (it is not the specific heat!)

Susceptibility of a more general spin system

Consider now a system containing N spin $1/2$ particles. Each is described by a variable $\sigma_i = \pm 1$. We assume the energy is

$$E(\sigma_1, \dots, \sigma_N) = -\mu_B B \sum_{i=1}^N \sigma_i + V(\sigma_1, \dots, \sigma_N) \quad (50)$$

where V describes some interaction between the spins.

The partition function is

$$Z = \sum_{\sigma_1, \dots, \sigma_N} e^{-\beta E(\sigma_1, \dots, \sigma_N)} \quad (51)$$

If the spins interact this cannot be factored as a product of independent terms. We will see an example of this later on.

Now, what we want is the magnetization, defined as

$$M = \langle \mathcal{M} \rangle, \quad \mathcal{M} = \mu_B \sum_{i=1}^N \sigma_i \quad (52)$$

So notice that we may write the energy (50) as

$$E(\sigma_1, \dots, \sigma_N) = -BM + V \quad (53)$$

Now we differentiate Z in (51) with respect to B :

$$\begin{aligned}\frac{\partial Z}{\partial B} &= \frac{\partial}{\partial B} \sum_{\sigma_1, \dots, \sigma_N} \exp\{\beta \mu B - \beta V\} \\ &= \sum_{\sigma_1, \dots, \sigma_N} \beta \mu \exp\{\beta \mu B - \beta V\}\end{aligned}$$

we therefore see that

$$\frac{1}{Z} \frac{\partial Z}{\partial B} = \beta \sum_{\sigma_1, \dots, \sigma_N} \mu \frac{e^{\beta E}}{Z} = \beta \langle \mu \rangle$$

Comparing with the free energy $F = -k_B T \ln Z$, we conclude that

$$M = - \frac{\partial F}{\partial B}$$

(54)

this formula is actually quite general.

the susceptibility, on the other hand, is

$$\chi = \frac{\partial M}{\partial B} = - \frac{\partial^2 F}{\partial B^2}$$

(55)

On the other hand, we may work this out explicitly:

$$\chi = -\frac{\partial^2}{\partial B^2} [-k_B T \ln z] = k_B T \left[\frac{z''}{z} - \left(\frac{z'}{z} \right)^2 \right]$$

where $z' = \partial z / \partial B$. Now:

$$\frac{z'}{z} = \beta \langle \mu \rangle$$

and

$$\frac{z''}{z} = \beta^2 \langle \mu^2 \rangle$$

Thus, we conclude that

$$\chi = \frac{1}{k_B T} \left[\langle \mu^2 \rangle - \langle \mu \rangle^2 \right]$$

(56)

Just like the heat capacity is actually the variance of the energy, we see now that the susceptibility χ is actually the variance of μ .

A nice feature of Eq (56) is that it allows us to compute χ even at $B=0$ (even though $\chi = \partial M / \partial B$).

Now comes a point I really want you to remember. If $v=0$ (no interactions) then the σ_i will be statistically independent. In this case $\text{Var}(X_1 + \dots + X_N) = \text{Var}(X_1) + \dots + \text{Var}(X_N)$ thus we get

$$\chi = \frac{\mu_B^2}{k_B T} \sum_{i=1}^N \left[\langle \sigma_i^2 \rangle - \langle \sigma_i \rangle^2 \right] \quad (57)$$

we can only do this when $v=0$. Please never forget that. When $v \neq 0$ the spins are no longer independent and we must use

$$\text{Var} \left(\sum_{i=1}^N \sigma_i \right) = \sum_{i=1}^N \text{Var}(\sigma_i) + \frac{1}{2} \sum_{i \neq j} \text{Cov}(\sigma_i, \sigma_j) \quad (58)$$

Let us try to reproduce Eq (49). when $B=0$ we have $\langle \sigma_i \rangle = 0$. Moreover, since $\sigma_i = \pm 1$, $\sigma_i^2 = 1$. Thus Eq (57)

becomes

$$\chi = \frac{\mu_B^2}{k_B T} \sum_{i=1}^N 1 = \frac{N \mu_B^2}{k_B T} \quad (59)$$

which is Eq (49). Success!