Notes for Lecture 8

Some examples of semi-classical ensembles

We have established quite a bit of statistical mechanics so far. Let us take a break for working on the formalism, and get acquainted with some typical examples, which illustrate the use of the ensemble idea.

8.1 Independent particles

We expect that for independent particles the probability distribution becomes simple. Indeed, the number of states, the partition function, etc. must become rather simple to evaluate.

Let us consider the partition function.

$$Z = \sum_{\mu} e^{-\beta\mathcal{E}} \tag{6.27}$$

For independent particles, we have[1]

$$\mathcal{E} = \varepsilon(\mu_1) + \ldots + \varepsilon(\mu_N) \tag{8.1}$$

$$\mu = (\mu_1, \mu_2, \ldots, \mu_N) \qquad \text{divide by } N! \text{ for counting, if identical} \tag{8.2}$$

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[1] By the second condition, $\mu = (\mu_1, \mu_2, \ldots, \mu_N)$, we mean that the counting of microstates can be independently performed for each particle, and then the total product can be taken. See Section 8.4.3 where this assumption is broken for Z. However, for that problem, this assumption remains valid for X!

where N is the number of particles, μ_i is the microstate for particle $i = 1, ..., N$, and $\varepsilon(\mu_i)$ is its energy. Therefore, we get

$$\begin{aligned} Z &= \sum_{\mu_1, \mu_2, \ldots, \mu_N} e^{-\beta \sum_i \varepsilon(\mu_i)} \\ &= \sum_{\mu_1, \mu_2, \ldots, \mu_N} e^{-\beta\varepsilon(\mu_1)} \ldots e^{-\beta\varepsilon(\mu_N)} \\ &= \frac{1}{A} \prod_{i=1}^{N} \sum_{\mu_i} e^{-\beta\varepsilon(\mu_i)} \end{aligned}$$

So, we arrive at an important result[2].

For independent particles in the semi-classical limit,

$$Z = \frac{1}{A} \prod_{i=1}^{N} Z_i \qquad Z_i : \text{the partition function for the } i\text{-th particle} \tag{8.3}$$

where A is the factor that divides out any double counting, in case when particles are indistinguishable. If all particles are distinguishable[3], then $A = 1$. If all particles are indistinguishable, then $A = N!$. If we have mixed groups of indistinguishable particles, then $A = \prod_j N_j!$, where N_j is the number of particles in each group.

Also, note that indistinguishable particles, by definition, will have the same dynamics, and their individual partition functions will be the same. Even distinguishable particles, if they are identical particles subjected to the same Hamiltonian, will have the same individual partition functions. In these cases, the product of individual partition functions will be simply the N_j-th power of an individual particle.

As a special case, we have

$$Z = \frac{1}{N!} Z_1^N \tag{8.4}$$

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[2] After all the talks about the decisive role that the large number of particles play in statistical mechanics, it might seem a bit weird to define such thing as a partition function for *one* particle (Z_i). There is actually nothing wrong with it. Review the theory of any canonical ensembles, with a single particle system in contact with a reservoir in mind. For such a system, a partition function continues to be perfectly well defined. Of course, all thermodynamic properties of such a small system will fluctuate wildly. But, keep in mind that a single-particle partition function introduced here is a simple device that we use to get to the N particle partition function, and so there is no real issue.

[3] Note that identical particles that are fixed in space, and well separated from one another, *are* distinguishable.

if all particles are indistinguishable. This is the case for the ideal gas problem. For the monatomic ideal gas problem, we found that

$$Z_1 = \frac{V}{\lambda^3} \qquad \text{single particle; no internal motion; classical limit} \tag{8.5}$$

as we can verify from Eq. 6.44, or as we can derive directly from Eq. 6.41. $\lambda = \lambda(T)$ is the thermal de Broglie wave length as defined in Eq. 6.43.

The above results are *not* applicable to the quantum case, for indistinguishable particles. While Eq. 6.27 is applicable to the quantum case, of course, none of the results for independent particles are applicable to the quantum case, if they are indistinguishable. This is because the quantum statistics of particles must be considered fully for the quantum case, which we have not done here. In the above, a very approximate consideration, just enough for the semi-classical case has been made, to obtain the $N!$ (or the $\prod_j N_j!$) factor.

But not all is lost. For the quantum case, we shall see later on that it is the *grand partition function* that factors out very nicely for indistinguishable particles and makes our life very easy.

8.2 Semi-classical or quantum?

Below, we shall study some typical examples of semi-classical statistical mechanics. Some examples may look like quantum examples. However, let us remember and further reflect upon the following point. As far as the statistical mechanics is concerned, one must realize, as we have been doing so far, that semi-classical statistical mechanics already includes the following quantum effects (cf. Sections 5.3 and 6.2.1).

1. Orbit quantization (Eq. 5.2; Bohr-Sommerfeld quantization) and the corresponding energy quantization.
2. Indistinguishable particle nature of identical particles, when they come into contact. However, we assume that the probability that two particles will occupy the same state is vanishingly small. This is the reason why the double-counting compensating factor, A, as defined above is $N!$ (or $\prod_j N_j!$), not some multinomial coefficient like $N!/(n_1! \ldots n_m!)$.

So, with this understanding, note that just because energy levels are quantized does not mean that we have a quantum statistical mechanics. Also, just because particles mix every now and then and emerge as indistinguishable particles do not mean that we have a quantum statistical mechanics. What matters, then?

The real distinction between the semi-classical statistical mechanics and the quantum statistical mechanics is hinted already by the above point 2. In quantum statistical mechanics, two particles can overlap in the same state with a significant probability and so **the quantum entanglement** of the many wave function becomes a crucial factor.

8.3 Ideal gas

8.3.1 Temperature, density, chemical potential

Let us consider a monatomic ideal gas, as before (Section 6.3.4). With

$$\lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}} \tag{6.43}$$

we have, as we already discussed above,

$$Z(T,V,N) = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \tag{6.44}$$

Using Sterling's approximation, we can rewrite this as

$$Z(T,V,N) \approx \frac{e^N}{N^N}\left(\frac{V}{\lambda^3}\right)^N = \left(\frac{e}{n\lambda^3}\right)^N \qquad N \gg 1. \tag{8.6}$$

It is important to note that (cf. Section 6.3.4) this semi-classical result is valid only when[4]

$$n\lambda^3 \ll 1 \qquad n \equiv \frac{N}{V} \quad \text{(particle number density)} \tag{8.7}$$

that is, at high temperature or low density. We considered already many standard quantities. Let us consider, in addition, the chemical potential μ. Using $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -k_B T \left(\frac{\partial \log Z}{\partial N}\right)_{V,T}$, we get $\mu = -k_B T(1 - \log(n\lambda^3) - 1)$.

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[4] You can justify this condition from the energy point of view, or from the wave function (wave packet, really) point of view. High thermal energy or small thermal wave length is the key to justify a classical mechanical particle like object.

In the semi-classical regime of ideal gas, we have:

$$e^{\beta\mu} = n\lambda^3 \quad \ll 1 \qquad\qquad \text{thus, } \frac{\mu}{k_B T} \to -\infty. \tag{8.8}$$

This regime occurs at high temperature or low density. The chemical potential is very large and negative in this regime, much larger in magnitude than the thermal energy $k_B T$.

8.3.2 Grand canonical ensemble view

Many particles

Let us consider the grand canonical partition function

$$Q(T,V,\mu) = \sum_{\mu} e^{-\beta(\mathcal{E}-\mu\mathcal{N})} = \sum_{\mathcal{N}} e^{\beta\mu\mathcal{N}} Z(T,V,\mathcal{N}) \tag{8.9}$$

If we use Eq. 8.6 then the logarithm of the summand becomes (for large $\mathcal{N}$),

$$f(\mathcal{N}) = \beta\mu\mathcal{N} + \mathcal{N}\left(1 - \log\frac{\mathcal{N}}{V} - 3\log\lambda\right) \tag{8.10}$$

We must maximize this in order find the most probable value of $\mathcal{N}$. $\left(\frac{\partial f}{\partial \mathcal{N}}\right)_{T,V} = \beta\mu + \left(1 - \log\frac{\mathcal{N}}{V} - 3\log\lambda\right) - 1 = 0$ gives

$$e^{\beta\mu} = n\lambda^3 \tag{8.8}$$

which, indeed, corresponds to the maximum of f since $f(\infty) = -\infty$. By combining Eqs. 8.6 and 8.9, and using the rule of large numbers, we get

$$Q(T,V,\mu) = e^{N} \tag{8.11}$$

$$\log Q(T,V,\mu) = N = \frac{Ve^{\beta\mu}}{\lambda^3} \qquad \text{the last step, using Eq. 8.8.} \tag{8.12}$$

This is quite as expected, since the grand potential

$$\Phi = -k_B T \log Q = -N k_B T \tag{8.13}$$

while, on the other hand, $\Phi = -PV$ for an extensive system, and thus, we establish, again, the equation of the state $PV = Nk_BT$. The central result in this exercise is Eq. 8.12. Let us look into this a bit deeper.

To prepare for the next topic, we shall not assume large N. So, instead of using Eq. 8.6 for Z, we choose to use Eq. 6.44, which is valid for *any* N (cf. footnote 2)[5]. Plugging it into Eq. 8.9, we get

$$Q(T,V,\mu) = \sum_{\mathcal{N}=0}^{\infty} \frac{1}{\mathcal{N}!}\left(\frac{Ve^{\beta\mu}}{\lambda^3}\right)^{\mathcal{N}} = \exp\left(\frac{Ve^{\beta\mu}}{\lambda^3}\right) \tag{8.14}$$

$$\log Q(T,V,\mu) = \frac{Ve^{\beta\mu}}{\lambda^3} = N \tag{8.12}$$

Hardly any particles

Consider a small volume of gas, where there is hardly any particle. The total volume of any dilute gas can be divided into many such small volumes. Clearly, counting number of particles in such a small volume, and repeating that counting many times, so as to account the total number of particles for the total volume, is just another Poisson statistics problem, assuming that particles are independent, as would be in an ideal gas.

Let us consider this $N \ll 1$ limit problem!

You might ask why we bother to do this. This "hardly any particle" setup seems like an interesting one, but do we really need it? Do we not already know everything that is to know about the ideal gas? Sure. However, it will turn out that this approach is very useful when we deal with a much more difficult problem—gas or fluid with inter-particle interactions. So, here we are preparing for that a little bit ahead of times.

By the way, the above point on Poisson statistics immediately makes it clear that, for an ideal gas, we must have

$$\Delta N = \sqrt{N} \tag{8.15}$$

That this is indeed so can be demonstrated easily by using Eq. 8.12 and Eq. 7.13 with $n = 2$ (left for your exercise).

Now, let us pursue the case of $N \ll 1$. In this case, we can use Eq. 8.14 and

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[5] Note that we are even considering the $\mathcal{N} = 0$ term very seriously here. You must convince yourself that $Z(T,V,\mathcal{N} = 0) = 1$, not just because Eq. 6.44 tells you so, but because physics tells you so.

examine only the first few terms. To the first approximation,

$$Q \approx 1 + \left(\frac{Ve^{\beta\mu}}{\lambda^3}\right) \tag{8.16}$$

$$\log Q \approx \frac{Ve^{\beta\mu}}{\lambda^3} = N \qquad \text{the last step from Eq. 7.13 with } n = 1. \tag{8.17}$$

So, we get the same result as before, already! Clearly, this first approximation is the only non-zero result in the current problem, as this small N expansion must connect to the exact solution obtained in Eq. 8.12. The only thing to keep in mind is that we are talking about a very small system here, and so all thermodynamic quantities are fluctuating wildly. However, this does not matter, as soon as we take N to be a large number, conceptually by adding all small volumes to get the original large volume. This corresponds to considering many variable PDFs (LN 4) and adding the measured values of N's for all small volumes. As we do so, N will become a value with a negligible fluctuation, and so will be other extensive variables. Intensive variables, which depend on ratios of extensive variables, will become certain as well.

While this transition from hardly any N to very large N is a physically very significant transition, there is hardly anything for us to do mathematically. All we need to do is to look at N and re-interpret it. So, there we have it—using the grand canonical ensemble, we have a way to deal with the ideal gas, be it extremely small or extremely large.

When interactions are included, the Poisson distribution argument will no longer be valid, since there will be correlations developing between particles. This is not of much consequence. On general grounds, we still expect that $\Delta N = O(\sqrt{N})$ (Section 7.3), while it most likely will not be exactly $\sqrt{N}$, and all arguments above continue to hold qualitatively.

8.4 Gibbs canonical ensemble examples

8.4.1 Ideal gas with a movable lid

To finish off our treatment of the ideal gas, let us consider this example. Normally, one considers the volume to be fixed. On the other hand, we can also consider the situation where the lid is movable. For the sake of simplicity, let us assume that this lid is freely movable without any friction. Let us assume that this lid does not have any mass. However, it is rigid, and it transmits the air pressure, which we take to be a constant value P, of the outside air. Also, we assume that the lid is conductive of heat, and so it transmits the temperature. We take the atmospheric temperature to be T.

Here, it is appropriate to consider the Gibbs ensemble. The Gibbs partition function

$$X(T,P,N) = \sum_{\mu} e^{-\beta(\mathcal{E}+P\mathcal{V})} \tag{8.18}$$

$$= \sum_{\mathcal{V}} e^{-\beta P\mathcal{V}} Z(T,\mathcal{V},N) \tag{8.19}$$

Using Eq. 6.44 for Z, and converting the volume sum to an integral, we get

$$X(T,P,N) = \frac{1}{v_0}\int_0^\infty d\mathcal{V} e^{-\beta P\mathcal{V}} \mathcal{V}^N \frac{1}{N!}\frac{1}{\lambda^{3N}}$$

where v_0 is the "volume quantum"[6]. The integral on $\mathcal{V}$ can be done easily, using $\int_0^\infty dx e^{-x} x^N = N!$. The result is[7]

$$X(T,P,N) = \frac{1}{v_0}\cdot\frac{1}{(\beta P\lambda^3)^N} \tag{8.20}$$

Taking the logarithm of this, we get

$$\log X = -N\log(\beta P\lambda^3) - \log v_0 = -N\log(\beta P\lambda^3) \tag{8.21}$$

where in the last step, the $O(1)$ term has been ignored in comparison to the $O(N)$ term. This means that the Gibbs free energy is given by

$$G(T,P,N) = -k_B T\log X = N k_B T\log\left(\beta P\lambda^3\right) = \mu N \tag{8.22}$$

where the last step comes from the extensivity assumption. Since $P\beta\lambda^3 = n\lambda^3$, it is clear to see that what we got is completely equivalent to Eq. 8.8 above. Had we started from scratch without knowing anything about various quantities about the ideal gas, we could have derived everything from this result on G and X.

So, we used the three canonical ensembles (grand canonical and Gibbs canonical in this lecture, canonical in Section 6.3.4) and the microcanonical ensemble (Section 6.2.2), to describe the ideal gas. It is important to see that any one of these treatments is completely equivalent to any other, in the thermodynamic limit ($N \to \infty, V \to \infty, N/V \to$ finite): as we have seen, they all produce the same results! We could have

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[6] This is actually not well-defined, in the current setup of the problem, but this will have no important consequence, as we will see shortly. If we include the mass of the lid, then its dynamics will make it possible to introduce a natural phase space quantum for the motion of the lid, resolving this issue.

[7] The power law exponent for $P\beta$ is $N+1$, not N, after integration. But, $N+1 \approx N$.

used any single one of them to derive all equilibrium thermodynamic functions that we like to know. Which one to use is largely based on the convenience. If one is faced with a general problem and is unsure how to start the problem, it is generally a good bet that either the canonical ensemble or the grand canonical ensemble will provide the most economical path to results.

8.4.2 Local magnetic moments, Curie susceptibility

Consider a magnetic moment of an ion that is fixed in space. Such object is common in any solid, when there is a small amount of magnetic impurities. What is the thermodynamics of such a magnetic moment?

To be definite, let us consider a local magnetic moment, $\vec{\mu}$. In the presence of a magnetic field $\vec{H} = H\hat{z}$, the Hamiltonian, $\mathcal{H}$, is given by

$$\mathcal{H} = -\vec{\mu}\cdot\vec{H} = -\mu_z H \tag{8.23}$$

The magnetic moment of an ordinary magnetic ion arises mostly from the electron spin, while the orbital angular momentum can play a role as well. In general, in the low field limit[8], one can write[9]

$$\mu_z = g\mu_B J_z \tag{8.24}$$

where g is the so-called Landé g factor (2 for pure spin magnetic moment) and

$$\mu_B = \frac{e\hbar}{2mc} = 5.789\times 10^{-9}\ \text{eV/gauss} \qquad \text{Bohr magneton} \tag{8.25}$$

where it is noted that 10,000 gauss (cgs unit) is equal to one Tesla (SI unit). Finally, $J_z\hbar$ is the z component of the total angular momentum ($J_z = -J, -J+1, ..., J$, where $\sqrt{J(J+1)}\hbar$ gives the magnitude of the total angular momentum).

While this problem looks like a quantum problem, and it definitely is, it nevertheless is a semi-classical *statistical mechanics* problem as we defined in Section 8.2.

It is very common to consider this problem as a canonical ensemble problem. Why this may be is easy to understand. Well, we got the above Hamiltonian, and its eigenvalues are easy to write down.

$$\epsilon(J_z) = -g\mu_B J_z H \qquad J_z = -J, -J+1, ..., J \tag{8.26}$$

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[8] For most not so light atoms, this low field limit is valid.

[9] Note the sign convention here. $g > 0$ and $\mu_B > 0$. For electron, note that μ_z is opposite to its total angular momentum. So, J_z would be the *negative* of the usual angular momentum.

Clearly, all we have to do is to calculate the "partition function"

$$X = \sum_{J_z} \exp(-\beta\epsilon(J_z)) = \sum_{J_z} \exp(\beta g \mu_B J_z H) \tag{8.27}$$

$$= \sum_{\mathcal{M}} \exp(\beta \mathcal{M} H) \qquad \mathcal{M} \equiv \mu_z = g\mu_B J_z \tag{8.28}$$

as each possible J_z value defines a microstate.

However, one must realize that, what we have is really a **Gibbs canonical ensemble**. Why so? If one reviews the theory that we have established so far (cf. box in page 4 of LN 7), one sees that the energy random variable $\mathcal{E}$ was meant to be the *internal energy* of the system, which *must not* depend on reservoir parameters. It represents the system's energy value that depends on (transient non-equilibrium) parameters of the system only. The parameter that we wrote as $\epsilon(J_z)$ on the other hand depends on H, the field applied externally. This H field is analogous to the atmospheric pressure in the previous problem. Both (H and $-P$) are examples of J_R (in box in page 4 of LN 7) that the reservoir enforces for the equilibrium state of the system.

What is the energy $\mathcal{E}$ for the current problem, then? It is zero. This is because the local magnetic moment that we are considering has no other dynamics than the response to the external field. Contrast this to the case of a gas, coupled to an external pressure as discussed in the previous example. In that case, even without the external pressure, the gas system has its own dynamics and its energy will depend on its volume, for example. In the current example, however, the direction of the magnetic moment has no implication on an intrinsic energy of the magnetic moment; it is important only when coupled to the external H field[10].

The notation in the second form above, Eq. 8.28, of the Gibbs partition function makes this fact very clear. Here, $\mathcal{M} = \mu_z$ is the **magnetization**, induced by the magnetic field H. Following our established convention for random variables and average/most-probable value

$$M = \langle \mathcal{M} \rangle \tag{8.29}$$

where M is the average/most-probable value of the magnetization[11]. Some useful

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[10] This situation will change if we have a lattice of local magnetic moments, which have internal interactions. Such a problem is that of spontaneous magnetism, such as ferromagnetism and antiferromagnetism. We will treat this topic later, when it will become clear what the non-vanishing $\mathcal{E}$ term looks like for magnetic problems.

[11] Of course, this magnetization as of now is that due to just one magnetic moment. This would be tiny. In real experiments, there are many magnetic ions, and the sum of all magnetic moments due to them gives the magnetization. That is, M is an extensive variable just as V is. Note that H is intensive, just as $-P$ is.

thermodynamic identities are

$$\begin{aligned} dE &= TdS + HdM \qquad (8.30) \\ dG &= -SdT - MdH \qquad (8.31) \end{aligned}$$

with M the "displacement" (x) and H is the "force" (J).

Now, let us calculate things.

$$\begin{aligned} X &= \frac{\sinh\left(\beta\left(J+\frac{1}{2}\right)g\mu_B H\right)}{\sinh\left(\beta\frac{1}{2}g\mu_B H\right)} \qquad (8.32) \\ G &= -k_BT\log X \\ &= k_BT\left[\log\left\{\sinh\left(\frac{1}{2}\cdot\frac{g\mu_B H}{k_BT}\right)\right\} - \log\left\{\sinh\left(\left(J+\frac{1}{2}\right)\frac{g\mu_B H}{k_BT}\right)\right\}\right] \qquad (8.33) \\ M &= -\left(\frac{\partial G}{\partial H}\right)_T \\ &= g\mu_B\left[\left(J+\frac{1}{2}\right)\coth\left(\left(J+\frac{1}{2}\right)\frac{g\mu_B H}{k_BT}\right) - \frac{1}{2}\coth\left(\frac{1}{2}\cdot\frac{g\mu_B H}{k_BT}\right)\right] \qquad (8.34) \end{aligned}$$

It is customary to define the Brillouin function, $B_J(y)$, as

$$B_J(y) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}\cdot y\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}\cdot y\right) \qquad (8.35)$$

in terms of which the magnetization is written as

$$M = g\mu_B J B_J(\beta g\mu_B JH) = yB_J(y)\frac{k_BT}{H} \qquad y = \beta g\mu_B JH. \qquad (8.36)$$

Note that

$$B_J(y) = -\beta\left(\frac{\partial G}{\partial y}\right)_T \qquad (8.37)$$

Howe about the entropy S and other functions?

$$\begin{aligned} S &= -\left(\frac{\partial G}{\partial T}\right)_H \\ &= -k_B\beta G - k_B y B_J(y) = -k_B\beta(G+MH) \qquad (8.38) \\ F &= G + MH = -\frac{S}{k_B\beta} = -TS \qquad (8.39) \\ E &= F + TS = 0 \qquad (8.40) \end{aligned}$$

The last result is just as expected from our discussion above.

The magnetization and its magnetic susceptibility are of primary interest. For this, it is useful to note the following behaviors of the Brillouin function.

$$B_J(y) \rightarrow 1 \qquad y \rightarrow \infty \tag{8.41}$$

$$B_J(y) \rightarrow \frac{J+1}{3J} y + ... \qquad y \rightarrow 0 \tag{8.42}$$

$$B_J(y) \rightarrow \coth(y) - \frac{1}{y} \qquad \text{Langevin function} \tag{8.43}$$

The Langevin function limit describes a continuum model, i.e., the classical liimt of this problem. The limit $y \rightarrow \infty$ corresponds to the low temperature or high field limit. The limit $y \rightarrow 0$ corresponds to the high temperature or low field limit. Therefore,

$$M \approx g\mu_B J \qquad y \rightarrow \infty \tag{8.44}$$

$$M \approx \frac{g^2 \mu_B^2 J(J+1)H}{3k_B T} \qquad y \rightarrow 0 \tag{8.45}$$

Therefore, the magnetic moment saturates at high field or low temperature limit, while it follows a H/T behavior at high temperature or low field limit. The latter behavior is the so-called **Curie paramagnetism**. The **Curie susceptibility** is given by[12]

$$\chi(T) = \left(\frac{\partial M}{\partial H}\right)_T = \frac{g^2 \mu_B^2 J(J+1)}{3k_B T} = \frac{C}{T} \qquad y \rightarrow 0 \tag{8.46}$$

where $C = \frac{g^2 \mu_B^2 J(J+1)}{3k_B}$ is the Curie constant. This is a very important behavior to look out for in any susceptibility measurement, since it is a strong effect for just a bit of impurities! Another point to be made is the meaning of "high temperature" in this context. Even for a fairly large field such as a 10 Tesla field, $\mu_B H$ is merely 0.6 meV. Since k_B = 25.85 meV / 300 K, 0.6 meV corresponds to 7 K. For $gJ \sim 1$ (as would be for spin 1/2 for example), y would be very small even at temperature as low as 100 K! If the magnetic field is even lower (typically the case), then y can be very small even for a few K temperature. So, the "high temperature" mentioned above can be very low in practice!

Lastly, note that we have been using only one magnetic ion in this section. For a distribution of magnetic ions, all of which must be fixed in space, the extension of our results is quite trivial: multiply all extensive quantities (M, χ, G, S, F, ...) by N, the number of the same type of ions. This simple result is owing to what we discussed in Section 8.1: in the current case, X is the product of X_i's due to individual ions.

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[12] In previous notes, we have been using χ as the random variable corresponding to the general displacement variable x. Here, we use χ as the susceptibility. There is no worry that these two will ever appear in the same section, since x is replaced by M in a magnetism problem. In any case, please do not confuse them!

8.4.3 The Z point of view

A curious student may ask, "How do we derive everything from the partition function Z in the above example? It looks like it is not giving any significant answer, as it looks like $Z = 1$ or $2J+1$ with the energy being zero..."

Let us answer this. A short answer is that everything is fine, but the canonical ensemble approach is something of an unnatural thing to consider for this particular problem. Nevertheless, it must be possible to extract all quantities from that picture as well. Figuring this out brings up interesting clarifying points, and so let us proceed.

To make the problem simple, we shall consider only the spin 1/2 problem.

First of all, let us keep in mind that Z is appropriate when we know the total "displacement." This means knowing the total magnetization in the current case. What does this mean? For one ion, fixing the total magnetization gives a trivial result. The magnetization is either μ_B (spin down) or $-\mu_B$ (spin up) (see footnote 9). Each possibility corresponds to one eigenstate, and thus, it appears that the partition function is 1, no matter how we think about it. But, this is not all. **For a macroscopic system, a given magnetization $M = N_n \mu_B$ clearly means much more states!** So, for $Z = Z(T, M, N)$, we *cannot* think one ion, independently, since the counting of μ states is not an unrestricted sum (cf. footnote 1). $\mu \neq (\mu_1, \mu_2, ..., \mu_N)$, but we must obey the condition that $\frac{N+N_n}{2}$ spins are down and $\frac{N-N_n}{2}$ spins are up, to conserve M. Thus, Z must be considered globally, due to this constraint in counting. This is all we have to do, since the **energy *is* really zero**, as we discussed all along. So, we simply get

$$Z = \frac{N!}{(\frac{N-N_n}{2})!(\frac{N+N_n}{2})!}. \tag{8.47}$$

Now, taking the logarithm and using Sterling's approximation, we get

$$\log Z = N \log N - \left(\frac{N-N_n}{2}\right) \log\left(\frac{N-N_n}{2}\right) - \left(\frac{N+N_n}{2}\right) \log\left(\frac{N+N_n}{2}\right). \tag{8.48}$$

Now, let us do this problem, just as we did in the previous section, using X and G. For this problem, the "Hamiltonian" $\mathcal{H} = -\mu_B \sigma_z H$, where $\sigma_z = \pm 1$ (we used $g = 2$ and defined $S_z = \sigma_z/2$). The following results are produced immediately. Note that, we consider N localized spins explicitly, *not* a single localized spin, for the reason that is explained above.

$$\begin{aligned}
X &= (2\cosh(\beta\mu_B H))^N && (8.49)\\
G &= -Nk_BT\left(\log 2 + \log\cosh(\beta\mu_B H)\right) && (8.50)\\
M &= -\left(\frac{\partial G}{\partial H}\right)_T = N\mu_B \tanh(\beta\mu_B H) && (8.51)\\
S &= -\left(\frac{\partial G}{\partial T}\right)_H = Nk_B\left\{\log 2 + \log\cosh(\beta\mu_B H) - \beta\mu_B H\tanh(\beta\mu_B H)\right\} && (8.52)\\
F &= G + MH = -TS && (8.53)\\
E &= F + TS = 0 && (8.54)\\
\log Z &= -\beta F = \frac{S}{k_B} = N\left\{\log 2 + \log\cosh(\beta\mu_B H) - \beta\mu_B H\tanh(\beta\mu_B H)\right\} && (8.55)
\end{aligned}$$

Let us show that Eqs. 8.55 and 8.48 are equivalent. First, we note that $N\tanh = N_n$ (we shall omit arguments for hyperbolic functions, for brevity). Second, note that $\cosh = \sqrt{\frac{1}{1-\tanh^2}} = \frac{N}{\sqrt{N^2-N_n^2}}$. Third, note that $\tanh^{-1}(z) = \frac{\log(1+z)-\log(1-z)}{2}$, which can be used to convert $\beta\mu_B H$ to a function of N_n/N. Using these three pieces of math, it takes some simple algebra to express Eq. 8.55 as a function of only two parameters, N and N_n, to verify that it is indeed equal to Eq. 8.48.

This completes the proof. Now, from Eq. 8.48, it should be possible to derive all quantities again. Before doing so, we must make sure to express $N_n = M/\mu_B$. Once we have done that, we then see that $\log Z$ is a function of M and N only. As N has no dynamics, we can omit it, considering only two independent variables. $F = -k_BT\log Z$. $S = -\left(\frac{\partial F}{\partial T}\right)_M$. $H = \left(\frac{\partial F}{\partial M}\right)_T$. $E = 0$ (since Z is T independent, or by definition!).

Question for you to answer: Since $E = 0$, it appears that we are in trouble—e.g., how do we calculate T? Actually, we are not in trouble. You must go back to the fundamental principle of the energy conservation $dE = TdS + HdM$ and then you can derive what T is, even when $dE \equiv 0$, as in the current case.

The Z point of view for the general J case is left for your (very) optional work—the counting of states becomes complicated.

8.5 Einstein phonons

Now, consider a lattice of ions. We shall assume that each ion is bound to each site by a Harmonic potential (Hooke's law), and there is no coupling between each ion to any other ions. This is the so-called **Einstein phonon** problem. Each ion is fixed at the lattice site, and well-separated from one another, and so they are distinguishable. Assuming that each lattice site is equivalent, then the total partition function is simply (cf. Section 8.1) given by $Z = Z_1^N$, where N is the number of ions, and Z_1 is the partition function for one ion.

So, we consider a simple harmonic oscillator problem, to get Z_1. However, for convenience, we will use Z, not Z_1, for the partition function of a single oscillator. Like in the previous example, we can scale all extensive quantities by N, to get the many oscillator quantities. Let us assume that the natural frequency of the oscillator is ω.

From the elementary quantum mechanics, we know that

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega \tag{8.56}$$

is the energy eigenvalues for this system.

Note that even for a single ion, we have three different polarizations. The ion can oscillate in three different directions. We shall focus on only one of the three polarizations. This means that our results on extensive quantities must be multiplied by $3N$, not N, to account for many oscillators at the end.

The computation of the partition function for one oscillator is simple.

$$Z = \sum_{n=0}^{\infty} \exp\left(-\beta\hbar\omega\left(n + \frac{1}{2}\right)\right) \tag{8.57}$$

$$= \frac{\exp\left(-\frac{\beta\hbar\omega}{2}\right)}{1 - \exp\left(-\beta\hbar\omega\right)} \tag{8.58}$$

From which

$$E = -\frac{\partial \log Z}{\partial \beta} = \frac{\hbar\omega}{2} + \hbar\omega\, n_P(\omega) \tag{8.59}$$

$$n_P(\omega) = \frac{1}{\exp(\beta\hbar\omega) - 1} \tag{8.60}$$

The interpretation of this expression is simple and is very important. The term $\hbar\omega/2$ is the zero point energy, or the quantum fluctuation energy, term. It arises due to the Heisenberg uncertainty principle.[13] The function $n_P(\omega)$ is the occupation number of "oscillation quanta." This oscillation quantum is what we call a photon, a phonon, or a molecular vibration, in a suitable context. Here, it is the Einstein

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[13] The zero point energy should not be considered just a constant, having no physical consequence. Its modification due to boundary conditions imposed by neutral matters in vacuum accounts for the (familiar) van der Waals force and the Casimir force.

phonon, where phonon means lattice vibration. **Later on, we will learn that each vibrational mode in quantum mechanics means a boson mode, where the boson corresponds to the vibration quantum.** It is a boson, since many quanta can co-exist ($n > 1$ is perfectly fine). Note that

$$n_P(\omega) = \langle n \rangle \tag{8.61}$$

where n is the quantum number in Eq. 8.56. Here, n is the number of bosons, i.e., **Einstein phonons**. Taking the temperature derivative of E, we get

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \ldots = k_B \frac{(\beta\hbar\omega)^2}{4\sinh^2\frac{\beta\hbar\omega}{2}} \tag{8.62}$$

From this it follows that

$$C_V \to \begin{cases} k_B\,(\beta\hbar\omega)^2\,\exp(-\beta\hbar\omega) & T \to 0,\ \text{Quantum regime, Activated behavior} \\ k_B & T \to \infty,\ \text{Du-Long Petit law, Equipartion} \end{cases} \tag{8.63}$$

Why is $C_V = k_B$ expected from the equipartition theorem? For a simple harmonic oscillator moving in one direction, the Hamiltonian is the usual one: $\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}kx^2$, for which the energy eigenvalue is as given in Eq. 8.56. $\mathcal{H}$ has two quadratic degrees of freedom (p and x), and so the equipartition energy is $\frac{2}{2}k_BT = k_BT$. So, the heat capacity is k_B.

What was surprising when Einstein proposed this theory was that, at low T, C_V does go to zero! It is turned on when $T \sim \hbar\omega/k_B \equiv \theta_{vib}$ is the vibrational temperature scale (which can be as much as 1000 K, easily). Historically, Einstein's theory was a bold proposal to explain the "specific heat puzzle" that confronted physicists at the turn of the last century. While this theory has these strong merits, it actually does not explain the low temperature data very well. This deficiency had to be fixed by the so-called Debye model. Nevertheless, the Einstein phonon model remains to be one of the most useful models for describing certain lattice vibrational modes, called optical phonons.