# II

# Statistical Mechanics of Simple Systems

# 7. Introduction

Up to now, everything you have done was:
- fairly general and abstract: you talked about systems, maximisation of entropy under constraints, or
- applied to $pV$ systems (ideal gas).

The goal of these lectures on simple systems is to show you how powerful the Statistical Mechanics approach is by applying it to (relatively) simple (but still very useful), non-$pV$ systems

The systems in question will conserve number of particles $N$ and volume $V$ (fixed external parameters) but will be in thermal contact with a thermostat (or heat bath) at fixed temperature $T$, with which they can exchange energy. In other words, the natural starting point to study them will be the canonical ensemble partition function:

$$\mathcal{Z}(\beta) = \sum_{\alpha} \exp(-\beta \epsilon_{\alpha}) \quad \text{with} \quad \beta = \frac{1}{k_B T} \tag{7.1}$$

which we interpret as the number of micro-states available to a system at a given temperature.

Why is the partition function of a system so important? Well, it contains all the information about the energy of the micro-states of the system, and you have seen that all thermodynamical equilibrium properties of the system can be derived from it, i.e. *all* the usual functions of state, including the equation of state, and heat capacity!

Why is this Statistical Mechanics approach so powerful? Well, if I give you the equation of state of one mole of ideal gas, $pV = RT$, and ask you what the heat capacity of the gas is at constant $V$, what would you answer? $3R/2$? That would be correct for a mono-atomic gas, but how do you know that the gas is mono-atomic? Its equation of state says nothing about that, but $\mathcal{Z}$ does!

Is it surprising? Well, not really. To construct $\mathcal{Z}$, you need to know all the quantum energy levels of a system. And what else is there to know? In general solving Shrödinger's equation for a complex system and getting its complete energy level spectrum is impossible, but one can do it for useful simple systems, and that is the subject of the next three lectures.

The path we will systematically follow to study these simple systems consists of three steps:

1. derive the single-particle partition function, $\mathcal{Z}_1$, being careful about any *level degeneracy*

2. combine the single-particle partition functions together to get the total partition function of the system, $\mathcal{Z}$, being careful as to whether the particles are *distinguishable or not* and can be considered as *independent or not*

3. derive the thermodynamical properties of the system from $\mathcal{Z}$

# 8. Paramagnetic solid

Consider a crystal of $N$ identical atoms (or ions), each in a particular position, in equilibrium with a heat bath at temperature $T$. Since the atoms are localised, we can apply the statistics of distinguishable particles, even though these atoms are of the same kind. When no external magnetic field is present, virtually all the atoms of the crystal are in their fundamental state[*].

Let us call $\vec{J}$ the *total angular momentum* of an atom, i.e. the sum of the *total orbital angular momentum*, $\vec{L}$, and *total spin*, $\vec{S}$, of all its electrons, in its fundamental state. From your Quantum Mechanics lectures, you know that to this total angular momentum is associated a magnetic moment[†]:

$$\vec{\mu} = -g_J \mu_B \, \vec{J} \tag{8.1}$$

where

$$g_J = \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{8.2}$$

is called the *Landé factor*[‡], $J$ can take integer or half-integer values and $\mu_B = e\hbar/(2m_e)$ is the *Bohr magneton*, with $e$ the elementary charge, $\hbar = h/(2\pi)$ the *reduced Planck constant* and $m_e$ the rest mass of the electron. From this expression, it is clear that if $J \neq 0$, each atom possesses a permanent magnetic moment[§]. Again, from your Quantum Mechanics

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[*]To excite the electrons, $e^-$, of an atom, you need energies $k_B T \sim 1$ eV, i.e. temperatures around $10^4$ K, so the probability of finding an excited atom at room temperature is negligible.

[†]If you prefer, think of the classical picture of the $e^-$ "orbiting" the nucleus and thus creating a mini current loop which in turns creates the magnetic moment.

[‡]Although you will only study the spin-orbit coupling in detail when you take Atomic Physics or Condensed Matter in the 3$^{\text{rd}}$ year, you can already understand how such a factor comes about from your 2$^{\text{nd}}$ year Quantum Mechanics lectures, in particular the ones devoted to the resolution of the Stern-Gerlach experiment puzzle.

[§]Note that this is not the case for most materials. What exists in all materials (including those for which $J = 0$) is a *diamagnetic* effect (part of the 3$^{\text{rd}}$ year Condensed Matter course), where the $e^-$ re-organise in an attempt to cancel the external magnetic field $\vec{B}_{\text{ext}}$ (when present), but this effect is generally small. This is also referred to as *Lenz's law*.

lectures, this means that e.g. the $z-$component of $\vec{J}$, $J_z$, can take $2J+1$ eigenvalues between $-J$ and $+J$. In other words, the fundamental energy level of the atom is $2J+1$ degenerate.

In the absence of an *external* magnetic field, all the states with different $J_z$ will share the same energy level, and are thus equally likely to be populated. As the magnetic moment of each atom is proportional to $J_z$, the net magnetic moment of the crystal is nil. However, if we plunge our crystal in a *uniform*¶ external magnetic field, $\vec{B}_{\text{ext}} \neq \vec{0}$ aligned with the $z-$axis and pointing up, each atom is subject to the Hamiltonian:

$$H = -\vec{\mu} \cdot \vec{B}_{\text{ext}} = g_J \mu_B \, J_z B_{\text{ext}} \tag{8.3}$$

This lifts the degeneracy of the atoms fundamental state by splitting them into $2J+1$ regularly spaced energy sub-levels, between energies $-g_J \mu_B \, JB_{\text{ext}}$ and $+g_J \mu_B \, JB_{\text{ext}}$.

If the atoms in the crystal are sufficiently far from one another, the interaction between their magnetic momenta are negligible and they can be considered as *independent*. In that case, the magnetic properties of the crystal can be calculated from the model Hamiltonian:

$$\mathcal{H} = \sum_{i=1}^{N} H_i = -\sum_{i=1}^{N} \vec{\mu}_i \cdot \vec{B}_{\text{ext}} = \sum_{i=1}^{N} g_J \mu_B \, J_z^{(i)} B_{\text{ext}} \tag{8.4}$$

which is simply the sum of the individual atom Hamiltonians given by equation (8.3). The crystal thus exhibits a magnetic moment which is aligned with the external field $\vec{B}_{\text{ext}}$, hence the name *para*magnetism.

## 8.1  Spin $\frac{1}{2}$ paramagnet

This is the special case where $J = S = 1/2$ and $L = 0$. This yields $g_J = 2$, so that the fundamental level of the atoms is split into two sub-levels with energies $\epsilon = \pm \mu_B B_{\text{ext}}$ in the presence of the external magnetic field $\vec{B}_{\text{ext}}$ (see Fig. 8.1). So, taking the first step in
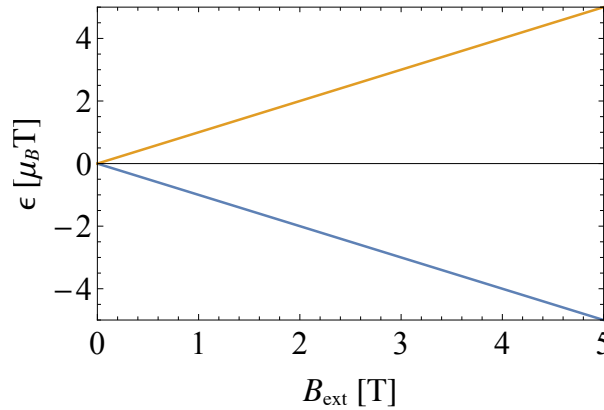


Figure 8.1: Sub-levels of energy split as a function of the external field strength, $B_{\text{ext}}$, with the blue line corresponding to magnetic dipoles pointing in the same direction as the field, and the orange line to dipoles pointing in the opposite direction. The zero point energy corresponds to the fundamental level in the absence of the field.

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¶In order to avoid complicating our life by having to evaluate potentially nasty integrals to obtains the average magnetic field present in the volume occupied by the crystal.

our three step procedure, we calculate the single-particle partition function of the system by summing these two *non-degenerate* energy sub-levels:

$$\mathcal{Z}_1 = \exp(-\beta\mu_B B_{\text{ext}}) + \exp(+\beta\mu_B B_{\text{ext}}) = 2\cosh\left(\frac{\mu_B B_{\text{ext}}}{k_B T}\right) \tag{8.5}$$

For the second step, recall that the atoms are *distinguishable* (because they are *localised*) *and independent*, so that the partition function of the system simply is the product of all the single-particle partition functions:

$$\mathcal{Z} = (\mathcal{Z}_1)^N \tag{8.6}$$

The third and final step consists in deriving the thermodynamical properties of the system from $\mathcal{Z}$. Let us start with the internal energy:

$$U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} = -N\mu_B B_{\text{ext}} \tanh\left(\frac{\mu_B B_{\text{ext}}}{k_B T}\right) \tag{8.7}$$

$U$ is plotted in Fig. 8.2 both as a function of $T$ (left panel) and $B_{\text{ext}}$ (right panel), arguably the main conclusion we can draw is that the internal energy of the crystal *increases* when it is plunged in an external magnetic field (right panel).
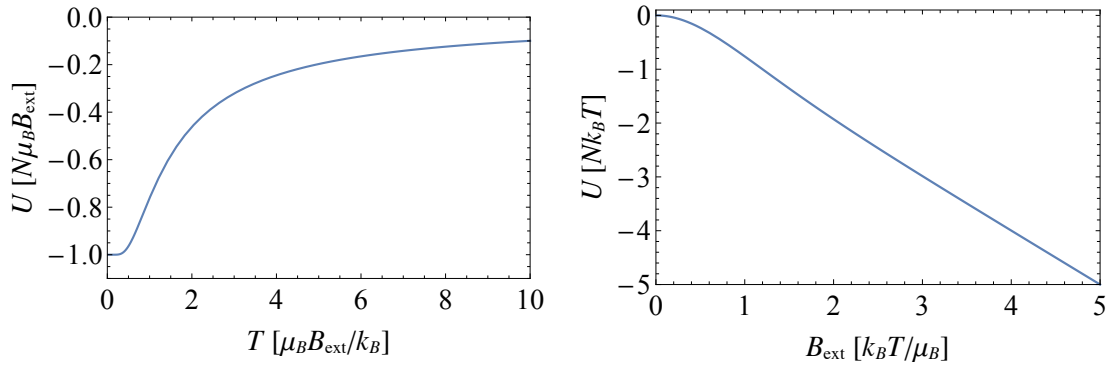


Figure 8.2: Internal energy of the paramagnet as a function of temperature $T$ (left panel) at fixed $B_{\text{ext}}$ and of the external field strength, $B_{\text{ext}}$ at fixed $T$ (right panel).

(R) We have not accounted for the internal energy contribution coming from other processes undergone by atoms in the crystal, such as vibrations. This will be the subject of the next lecture, and is only emphasised here to draw your attention on the arbitrariness of the energy zero point. We have chosen the internal energy of the crystal in the absence of an external field as zero, but of course the crystal has a non-nil internal energy in that case! In other words, only the difference in energy matters to study independent processes as the corresponding partition functions will simply multiply and the energies add up.

Looking at the left panel of Fig. 8.2 shows that at very low temperature and fixed $B_{\text{ext}} \neq 0$, $U = -N\mu_B B_{\text{ext}}$. This is exactly was we expect, the external field splits the level into two sub-levels, but at low $T$ *all* the atoms must be in the ground state, i.e. their lowest energy level $-\mu_B B_{\text{ext}}$, which directly leads to $U = -N\mu_B B_{\text{ext}}$. As the system is heated and its $T$ rises, some $e^-$ are excited to the upper energy level $+\mu_B B_{\text{ext}}$ and $U$ therefore increases. In the high temperature regime when $T \gg \mu_B B_{\text{ext}}/k_B$, the two sub-levels become very nearly

equally populated and the internal energy goes back to the original $U = 0$, i.e. to its value in the absence of the external magnetic field.

Now, at fixed $T$ (right panel of Fig. 8.2), for large $B_\text{ext}$, $\tanh(\beta\mu_B B_\text{ext}) \to 1$ and so $U \propto B_\text{ext}$. Again, this behaviour is expected: when $B_\text{ext}$ is large, the energy gap between sub-levels is so large that very few atoms can populate the upper energy sub-level, even though the system has a finite $T$, and so $U = -N\mu_B B_\text{ext}$ again. For weaker $B_\text{ext}$, the situation is a bit more complicated, as some $e^-$ are going to be thermally excited to the upper energy sub-level. However, in the regime $B_\text{ext} \ll k_B T/\mu_B$, $\tanh(\beta\mu_B B_\text{ext}) \to \beta\mu_B B_\text{ext}$ and we expect $U \propto -B_\text{ext}^2$.

What about the heat capacity[||]?

$$C_{B_\text{ext}} = \left(\frac{\partial U}{\partial T}\right)_{B_\text{ext}} = Nk_B \left(\frac{\mu_B B_\text{ext}}{k_B T}\right)^2 \frac{1}{\cosh^2\left(\mu_B B_\text{ext}/(k_B T)\right)} \qquad (8.8)$$

Looking at the high temperature regime, $T \to +\infty$ and for a fixed $B_\text{ext}$, we can derive a limit for $C_{B_\text{ext}} \simeq Nk_B\left(\mu_B B_\text{ext}/(k_B T)\right)^2 \to 0$. In the same way, the low temperature regime $T \to 0$, yields $C_{B_\text{ext}} \simeq Nk_B\left(2\mu_B B_\text{ext}/(k_B T)\right)^2 \exp\left(-2\mu_B B_\text{ext}/(k_B T)\right) \to 0$. We therefore predict a peak in the heat capacity of a paramagnet (see exercise 8.1 and Fig. 8.3 for detail)! Such a peak is actually observed in real systems: it is called the *Schottky* anomaly.
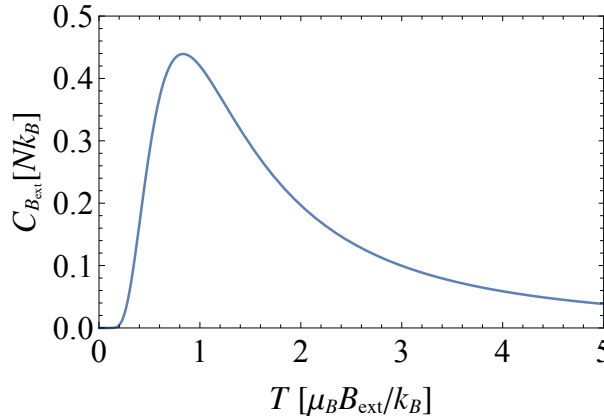


Figure 8.3: Heat capacity at constant external magnetic field for a spin half paramagnet. Note the presence of a peak centred on a specific temperature.

**Exercise 8.1** Estimate the temperature, $T_\text{max}$, and the heat capacity, $C_{B_\text{ext}}^\text{max}$ of a spin half paramagnet plunged in an external magnetic field $B_\text{ext}$.
**Ans:** $T_\text{max} \simeq 0.83\,\mu_B B_\text{ext}/k_B$, $C_{B_\text{ext}}^\text{max} \simeq 0.44 Nk_B$                                      ■

(R) What is the order of magnitude for the temperature at the peak? For this you need to know that it is difficult to manufacture magnets capable of producing a magnetic field much stronger than $B_\text{ext} \sim 10$ Tesla, so as the magnitude of $\mu_B$ and $k_B$ are similar, $T_\text{max} \sim 10$ K. The use of the Schottky anomaly plays an important role for cooling material at extremely low temperatures: if one can lower $B_\text{ext}$ without heat

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[||]Note that the volume of the crystal is fixed, so we are talking about heat capacity at constant $B_\text{ext}$ rather than constant $V$.

entering into the system, then $T$ has to decrease proportionally for the magnetisation to remain constant. In this way, you can go down from 10 K to the mK level and even lower with *nuclear* dipoles as you gain a factor $\sim 2000$ in mass when replacing $m_e$ in the Bohr magneton by $m_p$!

In general, the Helmholtz free energy will be more useful than any of the other thermodynamic potentials, because as you have already seen for the mono-atomic ideal gas and we will see time and again for other systems, it provides a direct route to their equation of state. The paramagnet is no different. Its Helmholtz free energy is:

$$\begin{aligned} F &= -k_B T \ln \mathcal{Z} \\ &= -N k_B T \ln \left( 2 \cosh \left( \frac{\mu_B B_{\text{ext}}}{k_B T} \right) \right) \end{aligned} \tag{8.9}$$

Now to the equation of state. For an ideal gas, it would be obtained by taking the partial derivative of $F$ with respect to the volume at constant temperature, as $\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V$. For a paramagnet, its *total magnetic moment*, $\vec{m} \equiv \sum_{i=1}^{N} \vec{\mu}_i$, will play the role of $p$ and (as we have already noted for the heat capacity), $\vec{B}_{\text{ext}}$ will play the role of $V$, even though given the intensive and extensive nature of these variables, one would naively have expected the reverse. In other words, we will write** $\mathrm{d}F = -S\,\mathrm{d}T - m\,\mathrm{d}B_{\text{ext}}$, so that its *magnetisation*

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**As we have seen in the Basic Thermodynamics lectures, "heat is heat but work differs". However, for magnetic systems, there is always some confusion about writing the work as $-\vec{m}\cdot\mathrm{d}\vec{B}_{\text{ext}}$ or $+\vec{B}_{\text{ext}}\cdot\mathrm{d}\vec{m}$. This confusion arises because the *total* magnetic field, $\vec{B}$, is the sum of the external field and the one induced in the paramagnet, i.e. $\vec{B} = \vec{B}_{\text{ext}} + \vec{B}_{\text{ind}}$. These fields are generated by current densities $\vec{J} = \vec{J}_{\text{ext}} + \vec{J}_{\text{ind}}$ and all three (total, external (free) and induced (bound)), obey Ampère's law, $\vec{\nabla} \times \vec{B} = \mu_0 \vec{J}$, where $\mu_0$ is the magnetic permeability in vacuum. To figure out the amount of work done *by* the crystal, we need to remove the contribution of the external field from the Hamiltonian of the system. Unfortunately, this task is not straightforward because Faraday's law requires that a back-electromotive force be generated in the device producing the *external* field when the *total* magnetic field of the system changes. In other words, work needs to be done to maintain the *external* current and field. This work, $\mathrm{d}W = -\mathrm{d}t \int \vec{J}_{\text{ext}} \cdot \vec{E}\,\mathrm{d}^3x$, integrates to $W = \mu_0^{-1} \int \vec{B}_{\text{ext}} \cdot \vec{B}\,\mathrm{d}^3x$ when the *total* field increases from $\vec{0}$ to $\vec{B}$, with the integrals performed over *all* space and using Maxwell-Faraday's equation $\vec{\nabla} \times \vec{E} = -\partial\vec{B}/\partial t$ to turn the electromotive force into a magnetic field. As such work maintains the *external* current, it is an energy which pertains to the surroundings and *not* to the paramagnet itself, so it should be *subtracted* from the total magnetic energy which permeates the crystal: $1/(2\mu_0) \int \vec{B}^2\,\mathrm{d}^3x$. By virtue of the same reasoning, we should also subtract the magnetic energy present in the crystal which is *entirely* due to the presence of the external field, i.e. $1/(2\mu_0) \int \vec{B}_{\text{ext}}^2\,\mathrm{d}^3x$ and $-\mu_0^{-1} \int \vec{B}_{\text{ext}}^2\,\mathrm{d}^3x$, where the second term corrects for our inclusion of the external field work to maintain the external current in $W$. So the *net* effect of the presence of an external field is to *add* $1/(2\mu_0) \int \vec{B}_{\text{ext}}^2\,\mathrm{d}^3x$ to the internal energy of the paramagnet, and therefore the magnetic (free) energy which should appear in the Hamiltonian of this latter is $F_{\text{mag}} = 1/(2\mu_0) \int (\vec{B}^2 - 2\vec{B}_{\text{ext}} \cdot \vec{B} + \vec{B}_{\text{ext}}^2)\,\mathrm{d}^3x = 1/(2\mu_0) \int (\vec{B} - \vec{B}_{\text{ext}})^2\,\mathrm{d}^3x = 1/(2\mu_0) \int \vec{B}_{\text{ind}}^2\,\mathrm{d}^3x$.

On the other hand, it is customary to describe the response of a paramagnet to the presence of an external magnetic field by its magnetisation $\vec{M}$, such that $\vec{\nabla} \times \vec{M} = \vec{J}_{\text{ind}}$, and to introduce an auxiliary field $\vec{H} = \vec{B}/\mu_0 - \vec{M}$, for which $\vec{\nabla} \times \vec{H} = \vec{J}_{\text{ext}}$. These quantities are therefore linked to the induced and external magnetic fields by $\vec{M}^{\perp} = \vec{B}_{\text{ind}}/\mu_0$ and $\vec{H}^{\perp} = \vec{B}_{\text{ext}}/\mu_0$ respectively, where the subscript $^{\perp}$ denotes the transverse component of the vector fields, with zero divergence (the curl free longitudinal components of $\vec{M}$ and $\vec{H}$ are generally not specified, unless $\vec{M}$ is a local function of $\vec{B}$). Now let the external magnetic field vary by $\mathrm{d}\vec{B}_{\text{ext}}$. Although the charged particles in the crystal (and therefore the *total* field $\vec{B}$) will respond to such a change, *at first order*, the variation in the paramagnet energy comes *entirely* from its dependence on $\vec{B}_{\text{ext}}$ (the crystal sits at a stable energy minimum in the external field so the other terms are of higher order). The magnetic energy term in the Hamiltonian of the crystal that we previously derived thus varies by $\mathrm{d}F_{\text{mag}} = -\mu_0^{-1} \int (\vec{B} - \vec{B}_{\text{ext}}) \cdot \mathrm{d}\vec{B}_{\text{ext}}\,\mathrm{d}^3x$ to first order. Skipping over the transverse component subtlety and identifying $\vec{M}$ with $\vec{B}_{\text{ind}}/\mu_0$ *inside* the crystal, we then obtain $\mathrm{d}F_{\text{mag}} = -\int_V \vec{M} \cdot \mathrm{d}\vec{B}_{\text{ext}}\,\mathrm{d}^3x = -\vec{m} \cdot \mathrm{d}\vec{B}_{\text{ext}}$. However, another possible choice is to consider the cross term $\vec{B}_{\text{ind}} \cdot \vec{B}_{\text{ext}}$ as part of the internal energy of the crystal (i.e. to remove the external field magnetic energy $1/(2\mu_0) \int \vec{B}_{\text{ext}}^2\,\mathrm{d}^3x$ from the paramagnet internal energy but regard the work done by the external current to maintain the field as part of it), thus writing the magnetic energy part in the Hamiltonian as

is given by[††]:

$$
\begin{aligned}
M &= -\frac{1}{V}\left(\frac{\partial F}{\partial B_{\text{ext}}}\right)_T \\
&= \frac{N\mu_B}{V}\tanh\left(\frac{\mu_B B_{\text{ext}}}{k_B T}\right)
\end{aligned}
\tag{8.10}
$$

In the limit of small external magnetic fields (or high temperatures), i.e. $\mu_B B_{\text{ext}} \ll k_B T$, this equation of state linking variables $M, B_{\text{ext}}$ and $T$ in a similar way as the ideal gas equation of state links $P, V$ and $T$, yields what is known as

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**Law 6 — Curie's law of paramagnetism.**

$$
M = \frac{N\mu_B^2 B_{\text{ext}}}{V k_B T}
\tag{8.11}
$$

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On the other hand, for large magnetic fields (or low temperatures), $\mu_B B_{\text{ext}} \gg k_B T$, all $e^-$ will be in the ground state with magnetic moments parallel to and pointing in the direction of the external magnetic field so that the magnetisation will *saturate* at $M = N\mu_B$.

Another quantity often used to describe materials is their *magnetic susceptibility*, $\chi$. It is a measure of the degree of magnetisation that the material will acquire when plunged in an external magnetic field. Magnetic susceptibility is a dimensionless quantity defined as:

$$
\chi \equiv \mu_0\left(\frac{\partial M}{\partial B_{\text{ext}}}\right)_T = \frac{\mu_0 N\mu_B^2}{V k_B T}\operatorname{sech}^2\left(\frac{\mu_B B_{\text{ext}}}{k_B T}\right)
\tag{8.12}
$$

In the paramagnet case, we then have $\chi > 0$ and, as we have already seen, the induced magnetisation increases the magnetic field in the crystal[‡‡]. Moreover, in the case of small external fields, $\chi = \mu_0 N\mu_B^2/(V k_B T)$, so it is inversely proportional to the temperature only, i.e. it does *not* depend on $B_{\text{ext}}$. Therefore, in this regime, where magnetisation is a linear function of the applied magnetic field (see equation (8.11)), one can rewrite the *total* field present in the crystal as $\vec{B} = \vec{B}_{\text{ext}}(1 + \chi)$.

Finally, the entropy of the spin half paramagnet is given by:

$$
S = \frac{U - F}{T} = -\frac{N\mu_B B_{\text{ext}}}{T}\tanh\left(\frac{\mu_B B_{\text{ext}}}{k_B T}\right) + N k_B \ln\left(2\cosh\left(\frac{\mu_B B_{\text{ext}}}{k_B T}\right)\right)
\tag{8.13}
$$

At high temperatures, $k_B T \gg \mu_B B_{\text{ext}}$, we have $S \to N k_B \ln 2$ and in the regime of low temperatures, i.e. $k_B T \ll \mu_B B_{\text{ext}}$, $S \to 0$. This is what we expect (from the arguably more intuitive microcanonical view of entropy), because at low $T$, *all* the $e^-$ should be in the lowest energy state and there is only one way for them to do so (1 micro-state associated), whilst at high $T$, each of the two individual states is equally likely to be populated (and thus there are $2^N$ possible ways of achieving this situation).

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$F'_{\text{mag}} = 1/(2\mu_0)\int(\vec{B}^2 - \vec{B}_{\text{ext}}^2)\,\mathrm{d}^3x = 1/(2\mu_0)\int(\vec{B}_{\text{ind}}^2 + 2\vec{B}_{\text{ind}}\cdot\vec{B}_{\text{ext}})\,\mathrm{d}^3x$ instead of $F_{\text{mag}} = 1/(2\mu_0)\int\vec{B}_{\text{ind}}^2\,\mathrm{d}^3x$. In this case, one arrives at the other result: $\mathrm{d}F'_{\text{mag}} = +\int_V \vec{B}_{\text{ext}}\cdot\mathrm{d}\vec{M}\,\mathrm{d}^3x = +\vec{B}_{\text{ext}}\cdot\mathrm{d}\vec{m}$. Both expressions for $\mathrm{d}F_{\text{mag}}$ and $\mathrm{d}F'_{\text{mag}}$ are correct, they simply depend on one's definition of the paramagnet internal energy: you now understand the source of the confusion for defining *infinitesimal* magnetic work! Note that we will use $\mathrm{d}F_{\text{mag}}$ in these lectures, as it is easier in practice to vary an external magnetic field than to control the magnetisation of a crystal. We will also drop the vector notation, thus implicitly assuming that the magnetic dipoles fully align with the external field.

[††]Strictly speaking, as we established in the previous footnote, the magnetisation is the magnetic moment of the paramagnet per unit volume, so we should define it as $\vec{M} \equiv \mathrm{d}\vec{m}/\mathrm{d}^3x$, where $\mathrm{d}\vec{m}$ represents the infinitesimal magnetic moment contained in the infinitesimal volume element $\mathrm{d}^3x$. However, as the system is assumed homogeneous, we simply write $\vec{M} = \vec{m}/V$, with $V$ the volume of the crystal.

[‡‡]Alternatively, if $\chi < 0$, the material will be called *diamagnetic* and the magnetic field permeating the material will be weakened by the induced magnetisation.
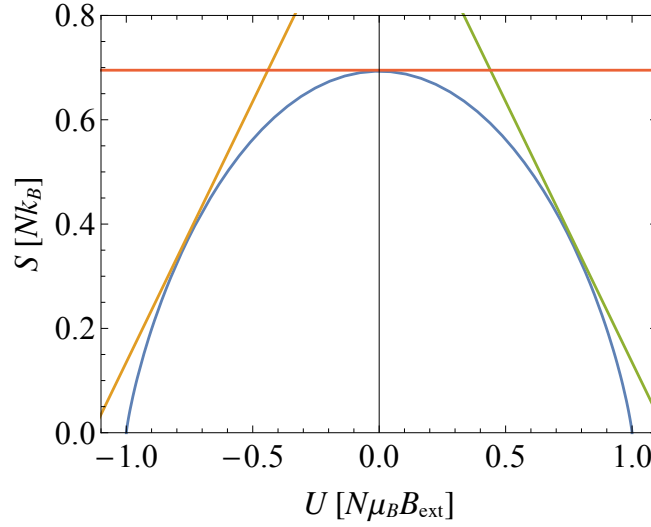
Figure 8.4: Entropy of a paramagnet as a function of internal energy for a fixed value of the external magnetic field. The temperature, $T = (\partial U/\partial S)_{B_{\text{ext}}}$, is given by the tangent to the curve at any point (orange, red and green lines). Note that this means $T$ is negative in the quadrant where $U > 0$ (green line see text for detail).

(R) From the thermodynamic definition of internal energy, $\mathrm{d}U = T\mathrm{d}S - M\mathrm{d}B_{\text{ext}}$, one readily obtains the temperature of the paramagnet as $T = (\partial U/\partial S)_{B_{\text{ext}}}$. Paramagnet entropy is plotted as a function of internal energy in Fig 8.4 for a system with $N$ magnetic dipoles. Starting from the system in its *minimal* internal energy state ($U = -N\mu_B B_{\text{ext}}$) and progressively increasing its temperature whilst maintaining a constant external magnetic field, one reaches $U = 0$ only for an infinite temperature (horizontal tangent in red). However, if one starts with the system in its *maximal* energy state, with all the dipoles parallel to the external field but pointing in the other direction, i.e. $U = +N\mu_B B_{\text{ext}}$, one realises that the system will spontaneously evolve towards $U = 0$ and infinite temperature, despite its temperature remaining *negative* (see slope of the green tangent to the curve in Fig 8.4) throughout the process! There is nothing wrong with this behaviour, which is in fact typical of systems with a *capped internal energy*. In such systems, the multiplicity of microstates *decreases* as one approaches the maximum internal energy allowed, so their entropy decreases as well. This underlines that the fundamental physical quantity is the entropy, governed by the second law of Thermodynamics, *not* the temperature which merely reflects the "willingness" of a system to give away energy: in that sense a system with negative temperature is simply *hotter* than a system with infinite positive $T$! A concrete example of a system for which negative temperatures have been measured is nuclear paramagnets which are prepared in the lowest internal energy state initially (strong external magnetic field, low positive temperature regime), before the applied magnetic field is "instantaneously" reversed (see Purcell E. & Pound R., Physical Review, 81, p279 (1951)).

## 8.2 General case paramagnet

In general, a paramagnet will have a total angular momentum $J > 1/2$, and therefore a different number of energy levels than the spin half paramagnet. For instance, if $J = 2$, then $J_z = -2, -1, 0, 1, 2$ and we have five levels of energy instead of two. Apart from this, the calculation of the thermodynamical properties of a general paramagnet follows the same exact route we have taken for the particular case of the spin half paramagnet. Its single-particle partition function is obtained by summing over all the *non-degenerate* energy

sub-levels:

$$\mathcal{Z}_1 = \sum_{J_z=-J}^{+J} \exp\left(-\frac{g_J\, J_z\, \mu_B B_{\text{ext}}}{k_B T}\right) = \frac{\sinh\left((J+1/2)\, R\right)}{\sinh(R/2)} \tag{8.14}$$

where the last equality results from evaluating the finite sum of terms of a geometric progression with common ratio $R = g_J\, \mu_B B_{\text{ext}}/(k_B T)$.

The atoms of the general paramagnet are *distinguishable* (because they are *localised*) *and independent*, so that, once again, the partition function of the system simply is the product of all the single-particle partition functions:

$$\mathcal{Z} = (\mathcal{Z}_1)^N \tag{8.15}$$

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**Exercise 8.2** Following what was done for the spin half paramagnet, derive $U, C_{B_{\text{ext}}}$ and $S$ from the partition function of the general paramagnet.
**Ans:**

$$U = -N g_J J \mu_B B_{\text{ext}} \left(\frac{2J+1}{2J}\coth\left(\frac{(2J+1)R}{2}\right) - \frac{1}{2J}\coth\left(\frac{R}{2}\right)\right)$$

$$C_{B_{\text{ext}}} = N k_B \left(\frac{g_J J \mu_B B_{\text{ext}}}{k_B T}\right)^2 \left(\left(\frac{1}{2J\sinh\left(R/2\right)}\right)^2 - \left(\frac{2J+1}{2J\sinh\left((2J+1)R/2\right)}\right)^2\right)$$

$$S = -\frac{N g_J J \mu_B B_{\text{ext}}}{T}\left(\frac{2J+1}{2J}\coth\left(\frac{(2J+1)R}{2}\right) - \frac{1}{2J}\coth\left(\frac{R}{2}\right)\right)$$
$$+ N k_B \ln\left(\frac{\sinh\left((J+1/2)\, R\right)}{\sinh(R/2)}\right)$$

∎

---

Leaving the calculation of the other thermodynamic properties of the general paramagnet as an exercise (8.2), we directly jump to its magnetisation:

$$\begin{aligned} M &= -\frac{1}{V}\left(\frac{\partial F}{\partial B_{\text{ext}}}\right)_T = \frac{k_B T}{V}\left(\frac{\partial \ln \mathcal{Z}}{\partial B_{\text{ext}}}\right)_T = \frac{g_J \mu_B}{V}\left(\frac{\partial \ln \mathcal{Z}}{\partial R}\right)_T \\ &= \frac{N g_J J \mu_B}{V}\, \mathcal{B}_J(RJ) \end{aligned} \tag{8.16}$$

where

$$\mathcal{B}_J(x) = \frac{2J+1}{2J}\coth\left(\frac{(2J+1)\, x}{2J}\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right) \tag{8.17}$$

is called the *Brillouin function* of order $J$ and is plotted for various values of $J$ in Fig 8.5. Note that for $J = 1/2$, the Brillouin function reduces to an hyperbolic tangent and we recover our spin half paramagnet result. Beyond this, in the large magnetic field/low temperature regime, $R \gg 1$, $\mathcal{B}_J \to 1$ and the magnetisation saturates as all the magnetic dipoles align with $\vec{B}_{\text{ext}}$. Conversely, for small external magnetic fields/high temperatures, $R \ll 1$ and $\mathcal{B}_J \simeq (J+1)R/3$ and we recover *Curie's law*:

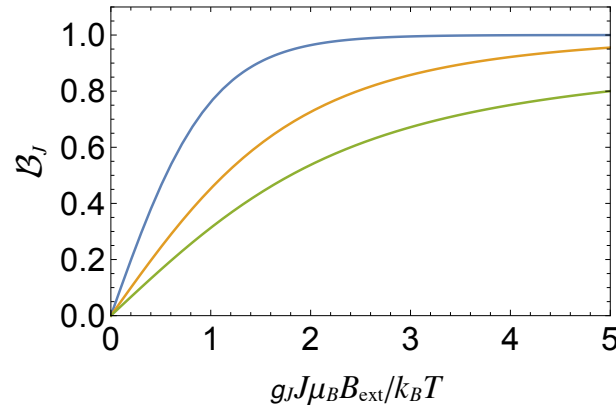$$M = \frac{N\, g_J^2\, J(J+1)\mu_B^2 B_{\text{ext}}}{3V k_B T} \tag{8.18}$$

Figure 8.5: Brillouin function of various orders $J$ as a function of the external magnetic field to temperature ratio, $R$. $J = 1/2$ in blue, $J = 2$ in orange and $J = \infty$ in green.

It turns out that $\mathcal{B}_J$ functions have been measured in the lab for crystals containing $Cr^{3+}$, $Fe^{3+}$ and $Gd^{3+}$ ions (see Henry W., Physical Review, 88, p559 (1952)). Note that these experiments are generally done at low temperatures as it is difficult to generate a strong external field to study the convergence to magnetisation saturation.

(R)   • $\mathcal{B}_\infty(x) = \coth x - 1/x$ is called the *Langevin function*, after french physicist Paul Langevin who explained paramagnetism (and diamagnetism) in 1905 *before* the emergence of Quantum Mechanics. This seems weird as one can actually prove (so called Bohr-van Leeuwen theorem) that *no* classical material can actually be magnetised (whether we are talking about para or diamagnetisation does not matter)! It turns out that Langevin got to the correct result because he had implicitly made the assumption that atoms were behaving like the Bohr atom in his derivation. Magnetisation is *purely* a quantum mechanical phenomenon.
• You will also hear about another kind of magnetism called *ferromagnetism* (and study it in the third year Condensed Matter course). This is the kind you are more likely to be familiar with, as it is "permanent", in the sense that ferromagnetic material continues to be magnetised after the applied external field has vanished. These ferromagnets include the common "fridge magnets". Essentially (restricting oneself to one domain/zone of the crystal where the magnetic field is aligned), ferromagnetism arises through the coupling of the spin of an atom with that of its neighbours: contrary to what we have seen for the paramagnet, the atoms *cannot* be considered independent. This coupling is generally modelled using a complicated *Heisenberg Hamiltonian* and it is customary to perform a mean field approximation (examples of which we will study in these lectures) to obtain a self-consistent implicit formula for the ferromagnet magnetisation: $M = N g_J \mu_B \tanh(g_J \mu_B B_{\text{eff}}/(2k_B T))/(2V)$ with $B_{\text{eff}} = B_{\text{ext}} + \lambda M$.

# 9. Simple harmonic oscillators

The goal of this lecture is to model the vibrations of atoms in a crystal. As for the paramagnet in the previous lecture, let us consider a crystal made of $N$ localised particles, so they are distinguishable even though they all are of the same kind. This crystal of fixed volume $V$ is in thermal equilibrium with a thermostat at temperature $T$, so that the canonical ensemble is the natural choice to derive its thermodynamical properties.

In the simplest model, also known as *Einstein's model*, all the atoms of the crystal are assumed to be vibrating as *independent* simple harmonic oscillators at the same frequency in all three spatial dimensions (see Fig. 9.1). It should seem a strange model, as interactions
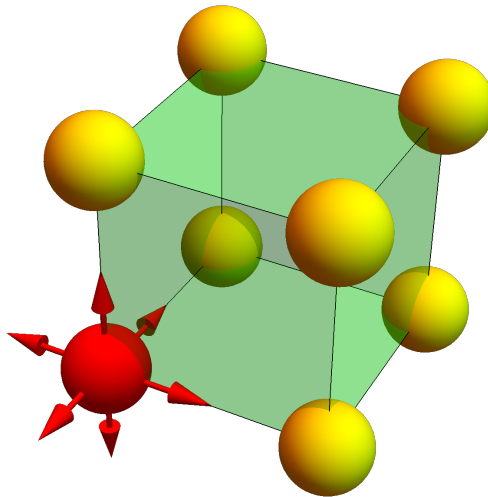


Figure 9.1: Schematic diagram of the three-dimensional vibrations (indicated by red arrows along the axes of symmetry) of atoms in a regular crystal.

between atoms *never* are negligible in solids. So why does the independent simple harmonic

oscillator model work at all? It is thanks to an approximation which is very commonly used in Statistical Mechanics: the *mean field* approximation.

To figure out how this approximation works, consider an atom that is part of the crystal. At zeroth order, it feels the $N - 1$ other atoms *globally*, through a mean potential energy, $U_{\text{mean}}(\vec{r})$, which depends on its own position in the crystal, $\vec{r}$, but *not* on the position of the other atoms. Let us then define the position of this specific atom, $\vec{r}$, with respect to its equilibrium position in the crystal and let us assume (to simplify things) that the mean potential it sits in is *isotropic*, i.e. $U_{\text{mean}}$ is only a function of the distance to equilibrium, $r$. As the atom will not stray very far from its equilibrium position in the crystal, let us expand $U_{\text{mean}}(r)$ around $r = 0$. This must be a *minimum* of the mean potential (necessary for the equilibrium to be stable), so we have:

$$\frac{\mathrm{d}U_{\text{mean}}(0)}{\mathrm{d}r} = 0 \quad \text{and} \quad \frac{\mathrm{d}^2 U_{\text{mean}}(0)}{\mathrm{d}r^2} \equiv \kappa > 0 \tag{9.1}$$

At lowest order in $r$, we can thus write:

$$U_{\text{mean}}(r) = -U_0 + \frac{\kappa}{2}r^2 \tag{9.2}$$

where $U_0$ is the (positive) binding energy per atom in the crystal. Under such an approximation, each atom constitutes an *independent* simple harmonic oscillator since its energy is:

$$\varepsilon = \frac{\vec{p}^2}{2m} - U_0 + \frac{\kappa}{2}r^2 = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + \frac{\kappa}{2}(x^2 + y^2 + z^2) - U_0 \tag{9.3}$$

where $m$ is the mass of the atom and $\vec{p}$ its momentum. The crystal is thus composed of $N$ such independent simple harmonic oscillators with the *same* angular frequency $\omega = \sqrt{\kappa/m}$.

## 9.1   The 1-D case

Before we embark upon the quest to solve the full three-dimensional case, let us assume that our simple harmonic oscillators can only oscillate in one dimension, say along the $z-$axis. We know from our Quantum Mechanics lectures that the solution of Schrödinger's equation in this case leads to the following spectrum of energy levels:

$$\epsilon_n = -U_0^{(1D)} + \left(n + \frac{1}{2}\right)\hbar\omega \tag{9.4}$$

where $n \in \mathbb{Z}^+$ is the level number, and $\hbar = h/(2\pi)$ the reduced Planck constant. Note that the superscript $^{(1D)}$ indicates that the potential minimum is different from that of the full three-dimensional case. In contrast to the paramagnet, you will notice that there is an *infinite* number of energy levels for the crystal. However, just like for a paramagnet, these energy levels are equally spaced which makes matters easier from a mathematical point of view.

Applying our now standard three step approach, we first derive the single-particle partition function of the crystal:

$$\mathcal{Z}_1 = \sum_{n=0}^{+\infty} \exp\left(\beta\left(U_0^{(1D)} - (n + 1/2)\hbar\omega\right)\right) \tag{9.5}$$

which is a geometric progression with an infinite number of terms so

$$\mathcal{Z}_1 = \exp\left(\beta U_0^{(1D)}\right) \frac{\exp(-\beta\hbar\omega/2)}{1 - \exp(-\beta\hbar\omega)} \tag{9.6}$$

Since the atoms in the crystal are distinguishable (localised) and independent, its partition function then reads:

$$\mathcal{Z} = (\mathcal{Z}_1)^N = \exp\left(N\beta U_0^{(1D)}\right) \left(\frac{1}{2\sinh\left(-\beta\hbar\omega/2\right)}\right)^N \tag{9.7}$$

Finally the third step consists in deriving the thermodynamical properties of the crystal. Its internal energy is:

$$
\begin{aligned}
U &= -\frac{\partial\ln\mathcal{Z}}{\partial\beta} \\
&= N\left(-U_0^{(1D)} + \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp\left(\hbar\omega/(k_BT)\right) - 1}\right)
\end{aligned} \tag{9.8}
$$

So when $k_BT \gg \hbar\omega$, $\exp\left(\hbar\omega/(k_BT)\right) \simeq 1 + \hbar\omega/(k_BT)$ and $U \simeq Nk_BT$, i.e. $U$ is independent of the properties of the oscillators! This is a consequence of the *classical theorem of equipartition of energy*, which we will state and demonstrate right now: when $k_BT \gg \hbar\omega$, our quantum harmonic oscillators behave like classical harmonic oscillators.

> **Theorem 9.1.1 — Classical theorem of equipartition of energy.** If the energy of a classical system is the sum of $N$ *quadratic* terms, and the system is in contact with a heat reservoir at temperature $T$, then the mean energy of the system is $\langle E \rangle = Nk_BT/2$.

*Proof.* Consider a system whose energy has a quadratic dependence on some variable and is interacting with a heat reservoir at temperature $T$. This system is thus able to borrow energy from its surroundings and give it back. What mean thermal energy $\langle E \rangle$ does it have? Mathematically, this means that the energy of the system has the form $E(x) = Ax^2$, where A is a positive constant, and $x$ is the variable[*]. Let us assume that $x$ can take any continuous value. As previously derived in the Statistical Mechanics lectures, the probability $p(x)$ of the system having a particular energy $Ax^2$ under the constraint of constant mean energy is given by:

$$p(x) = \frac{\exp(-\beta Ax^2)}{\int_{-\infty}^{+\infty} \exp(-\beta Ax^2)\,dx} \tag{9.9}$$

so that the mean energy of the system is:

$$
\begin{aligned}
\langle E \rangle &= \int_{-\infty}^{+\infty} E(x)p(x)\,dx \\
&= \frac{\int_{-\infty}^{+\infty} Ax^2\exp(-\beta Ax^2)\,dx}{\int_{-\infty}^{+\infty} \exp(-\beta Ax^2)\,dx} \\
&= \frac{1}{2\beta} = \frac{k_BT}{2}
\end{aligned} \tag{9.10}
$$

where we have integrated by parts the numerator and then simplified away the denominator in the resulting expression. This is a remarkable result: the mean energy of the system is *independent* of the constant $A$ and simply proportional to $T$! We leave it as an exercise to finish the proof, extending it to $N$ quadratic terms (also called *modes* or *degrees of freedom*) by writing the energy of the system as $E = \sum_{i=1}^{N} A_i x_i^2$. ∎

---

[*]This is a very common situation in Physics, where $x$ could be the velocity $v$, in which case the energy would be kinetic, or $x$ could be the displacement of a mass attached to a spring, etc ...

Back to our one dimensional simple harmonic oscillator, we can now calculate its heat capacity at constant volume:

$$
\begin{aligned}
C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\
&= N k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp\left(\hbar\omega/(k_B T)\right)}{\left(\exp\left(\hbar\omega/(k_B T)\right) - 1\right)^2}
\end{aligned}
\tag{9.11}
$$

R • Note the similarity of the heat capacity of the crystal with that of the paramagnet: the $+$ sign in the term at the denominator for the paramagnet has become a $-$ sign here for the crystal, but otherwise the expressions are the same, provided you replace $2\mu_B B_{\text{ext}}$ by $\hbar\omega$.

• In a real system, the heat capacities due to magnetisation and oscillations will add up as they are independent from each other! This is also true for their internal energies. We will see how this additivity property works in more detail when we discuss the polyatomic gas.

## 9.2  The 3-D case

As each of the three directions of oscillation is independent, we can simply write the energy level spectrum of the crystal as:

$$
\epsilon_{n_x,n_y,n_z} = -U_0^{(3D)} + \left(n_x + \frac{1}{2}\right)\hbar\omega + \left(n_y + \frac{1}{2}\right)\hbar\omega + \left(n_z + \frac{1}{2}\right)\hbar\omega
\tag{9.12}
$$

with $n_x, n_y$ and $n_z \in \mathbb{Z}^+$ and independent of one another. So the three-dimensional single-particle partition function reads:

$$
\mathcal{Z}_1^{(3D)} = \mathcal{Z}_1(x)\mathcal{Z}_1(y)\mathcal{Z}_1(z) = \left(\mathcal{Z}_1^{(1D)}\right)^3
\tag{9.13}
$$

and similarly, the three-dimensional partition function is equal to

$$
\mathcal{Z}^{(3D)} = \left(\mathcal{Z}^{(1D)}\right)^3
\tag{9.14}
$$

Furthermore, as all thermodynamical potentials are functions of $\ln \mathcal{Z}$, we can directly write:

$$
\begin{aligned}
C_V^{(3D)} &= 3\, C_V^{(1D)} \\
&= 3\, N k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp\left(\hbar\omega/(k_B T)\right)}{\left(\exp\left(\hbar\omega/(k_B T)\right) - 1\right)^2}
\end{aligned}
\tag{9.15}
$$

Defining the *Einstein temperature*, $T_E \equiv \hbar\omega/k_B$, one can see that it depends on the properties of the crystal through the angular frequency $\omega \equiv \sqrt{\kappa/m}$, i.e. it decreases with the mass of the atoms and increases with the "spring constant" $\kappa$.

R Note that $\kappa \equiv \mathrm{d}^2 U_{\text{mean}}(0)/\mathrm{d}r^2 \sim U_0/d^2$, where $d$ is the distance between two neighbouring atoms. This distance is constant (up to a factor 2-3) for all materials, so $\kappa$ is essentially a function of $U_0$, the depth of the potential well in which the atom is moving.

This leads to re-writing the three-dimensional heat capacity of the crystal as:

$$C_V = 3\,N k_B \left(\frac{T_E}{2T}\right)^2 \frac{1}{\sinh^2\left(T_E/(2T)\right)} \tag{9.16}$$

where we have dropped the $^{(3D)}$ superscript for the sake of notation simplicity. Focussing on the high temperature regime, $T \gg T_E$, we get $C_V \simeq 3Nk_B$, which is independent of both temperature and the nature of the crystal considered! This is the so-called *Dulong & Petit law* discovered in 1819, and which we now know is a consequence of the classical theorem of equipartition of energy. In the low temperature regime, $T \ll T_E$, we have that $C_V \simeq 3\,N k_B (T_E/T)^2 \exp(-T_E/T)$ and $\lim_{T \to 0} C_V = 0$.

These considerations lead to the plot of $C_V$ as a function of $T$ displayed in Fig. 9.2.
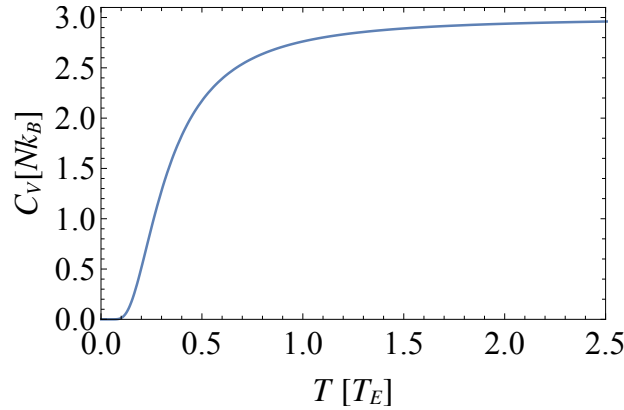


Figure 9.2: Heat capacity of a three-dimensional crystal due to atom vibrations, as a function of temperature.

(R) • The importance of this simple Einstein model of a crystal *cannot* be underestimated. Indeed, it explicitly shows that the decrease in the heat capacity of solids at low temperature is *purely a quantum phenomenon*, like magnetisation!

• If you adjust the Einstein temperature for each crystal, it approximately reproduces the change in heat capacity as a function of temperature for *real* solids (see Einstein A., Annalen der Physik, 22, p87 (1907)).

A few things are worth emphasising about the limitations of this simple crystal model. For those of you who are (rightly) worried about the infinite number of energy levels, it must be noted that at *very* high temperatures, $T \gg U_0^{(3D)}/k_B$, the thermal energy overcomes the binding energy of the crystal and this latter *melts*. However, even before this catastrophic outcomes takes place, at lower thermal energies, the quadratic expansion of the potential will no longer be a valid approximation, and we will need to take into account higher order terms to provide an adequate description of the atom motion. So why sum over an infinity of energy levels even when the temperature is reasonable then? The reason is that the infinite sum converges very rapidly. Indeed, you can easily convince yourself that *any* energy level with an energy $> k_B T$ has a *very low* probability of being excited, so using the full infinite sum is an excellent approximation of the physically correct truncated sum.

At the other end of the temperature range, the Einstein model, while qualitatively correct, is quantitatively wrong at low temperatures. Experiments show that the heat capacity of solids goes to zero as $C_V \propto T^3$ rather than exponentially. As previously remarked, this exponential decay is a direct consequence of the existence of a minimal excitation quantum $\hbar\omega$, which is non-nil for the simple harmonic oscillator. This is the subject of the exercise below.

**Exercise 9.1** Show that $C_V \propto \exp(-T_E/T)$ is an inevitable conclusion of the simple harmonic quantum oscillator model if $\hbar\omega \neq 0$. [ hint: write the first two lowest energy levels of the system, $\epsilon_0$ and $\epsilon_1$, which are, by definition, such that $\epsilon_1 - \epsilon_0 = \hbar\omega$ and use them to calculate $\mathcal{Z}$ in the very low $T$ limit.]

**Ans:** $C_V \simeq g_1/g_0 \big(\hbar\omega/(k_B T)\big)^2 \exp\big(-\hbar\omega/(k_B T)\big)$ when $T \ll \hbar\omega/k_B$, with $g_0$ and $g_1$ the degeneracy coefficients of levels 0 and 1 respectively. ∎

In other words, one can only hope to reproduce the experimental power law behaviour of the heat capacity at low temperatures if the energy level spectrum in the neighbourhood of the fundamental level, $\epsilon_0$, is almost *continuous*. The solution of this conundrum is to realise, as Debye did, that the existence of a unique frequency of oscillation, $\omega$, is linked to the assumption of *independence* of the oscillators. If one takes into account coupling terms, eigenfrequencies will differ from their initially identical values[†].

---

[†]Intuitively and physically, when an atom wanders away from its equilibrium position, it exerts a force on its neighbours, repelling those it is getting close to and attracting those it moves away from. These neighbours then act on their own neighbours and so on and so forth. So crystal vibrations are collective rather than individual at low temperature.

# 10. Polyatomic ideal gases

You have derived, in another part of the course, the partition function (and hence the thermodynamical properties) of the mono-atomic perfect gases. In this lecture, we will study the modifications that we need to introduce to describe an ideal gas composed of poly-atomic molecules*. Essentially, this means that we are going to take into account the *internal structure* of the gas particles instead of treating them as an ensemble of mathematical points. In other words, we will have to consider the extra degrees of freedom associated with the possibility that these particles/molecules can also vibrate and rotate ...

## 10.1 General case

Let us consider a gas of $N$ *identical, non-interacting* molecules of mass $m$, enclosed in a recipient of fixed volume $V$, in contact with a thermostat at temperature $T$. We will assume that $N$ is sufficiently large (so that the thermodynamic limit is reached), and that $T$ is sufficiently large† and $N/V$ sufficiently low (so that the mean occupation number of a single particle micro-state is low ($\ll 1$)).

> **R** This last assumption is also sometimes called the *Maxwell-Boltzmann approximation* as it yields the same partition function for bosons and fermions. The gas is therefore *classical* in the sense of *non-degenerate*.

We can then write the partition function of the gas as:

$$\mathcal{Z} = \frac{1}{N!} \mathcal{Z}_1^N \tag{10.1}$$

where the factorial of $N$ term accounts for the fact that particles are *indistinguishable* and $\mathcal{Z}_1$ is the *single-particle partition function*. Up to this point, this is identical to what you have seen for the mono-atomic gas.

---

*In truth, most of the lecture will focus on diatomic molecules for simplicity, but the way to generalise the results to molecules composed of more atoms will be outlined.

†Albeit lower than the ionization temperature of the gas ($T < 10^4$K).

Let us follow our three-step procedure and start with the first step of calculating $\mathcal{Z}_1$. As for the mono-atomic gas, the single particle Hamiltonian has a kinetic energy part, $\mathcal{H}_0 = \vec{p}^2/(2m)$, where $\vec{p}$ is the momentum of the particle, but also, and this is specific to poly-atomic gases, an internal structure part, which we won't make explicit for the moment and simply write as $\mathcal{H}_{\mathrm{int}}$[‡]. In other words, we will write the single particle Hamiltonian as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\mathrm{int}} = \frac{\vec{p}^2}{2m} + \mathcal{H}_{\mathrm{int}} \tag{10.2}$$

The internal degrees of freedom associated with $\mathcal{H}_{\mathrm{int}}$ are *independent* of the translational motion degrees of freedom associated with $\mathcal{H}_0$[§].

> (R)  Physically, you can understand this easily: it is only when molecules collide that a fraction of their translational kinetic energy can be transferred to rotational or vibrational internal motions (so called *inelastic* collisions). For ideal gases where collisions between particles are, by definition, ignored (*non-interacting* particles), such a coupling is thus neglected.

This means that a single-particle state, $\chi$, will be defined by a monochromatic wave function with wave vector $\vec{k} = \vec{p}/\hbar$ which describes the eigenstates of $\mathcal{H}_0$, as in the mono-atomic gas case, *and* the quantum numbers describing the eigenstates of $\mathcal{H}_{\mathrm{int}}$, i.e. the internal structure of the particle (including spin). In other words, if we label $\tau$ the ensemble of these internal structure quantum numbers, we have $\chi = \{\vec{k}, \tau\}$, and the corresponding energy levels are:

$$\varepsilon_\chi = \frac{\hbar^2 \vec{k}^2}{2m} + \epsilon_\tau \tag{10.3}$$

i.e. the sum of an eigenvalue of $\mathcal{H}_0$ and an eigenvalue of $\mathcal{H}_{\mathrm{int}}$ (called $\eta_\tau$ here). So we have, using the usual notation $\beta = 1/(k_B T)$:

$$
\begin{aligned}
\mathcal{Z}_1 &= \sum_\chi \exp(-\beta \varepsilon_\chi) \\
&= \sum_{\vec{k}} \sum_\tau \exp\left(-\beta\left(\frac{\hbar^2 \vec{k}^2}{2m} + \epsilon_\tau\right)\right) \\
&= \frac{V}{(2\pi)^3} \int \sum_\tau \exp\left(-\beta\left(\frac{\hbar^2 \vec{k}^2}{2m} + \epsilon_\tau\right)\right) \mathrm{d}^3 k \\
&= \frac{V}{(2\pi)^3} \int \exp\left(-\beta\frac{\hbar^2 \vec{k}^2}{2m}\right) \mathrm{d}^3 k \times \left(\sum_\tau \exp(-\beta \epsilon_\tau)\right) \\
&= V \left(\frac{m}{2\pi\hbar^2 \beta}\right)^{3/2} \times \xi(\beta)
\end{aligned} \tag{10.4}
$$

where $\xi(\beta)$ is the single-particle partition function associated with the internal structure of the particle and we have taken advantage of the high enough temperature to replace the discrete sum over $\vec{k}$ by a continuous integral. In what follows, we will evaluate it explicitly for a diatomic molecule composed of two different atoms, but notice that $\xi(\beta)$ is *independent* of $V$.

---

[‡]We proceed this way because, as you will see, it will allow us to derive important results regarding the thermodynamical properties of a polyatomic gas which hold *regardless of the gas specific composition.*

[§]If you prefer, in Quantum Mechanics parlance, the operators $\mathcal{H}_{\mathrm{int}}$ and $\mathcal{H}_0$ commute.

Having obtained $\mathcal{Z}_1$, we proceed to the second step of our procedure and calculate the partition function using equation (10.1):

$$\mathcal{Z} = \frac{V^N}{N!} \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3N/2} \xi^N(T) \tag{10.5}$$

Finally, in the third step, we derive thermodynamical quantities from $\mathcal{Z}$. As usual, we start with the Helmholtz free energy:

$$\begin{aligned} F &= -k_BT \ln \mathcal{Z} \\ &= -Nk_BT \left(\ln \frac{V}{N} + \frac{3}{2} \ln \frac{mk_BT}{2\pi\hbar^2} + 1 + \ln \xi(T)\right) \end{aligned} \tag{10.6}$$

where the final equality made use of the Stirling formula, $\ln N! \simeq N \ln N - N$.

(R) If you replace $\xi$ by $2s+1$, you recover the mono-atomic case, as the spin $s$ is the only internal degree of freedom of an atom.

$F$ for a polyatomic gas has the same dependency on $V$ than the mono-atomic gas $F$ so

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_BT}{V} \tag{10.7}$$

meaning the ideal gas equation of state is valid *no matter* the internal structure of the molecules that compose it! However, the internal energy,

$$\begin{aligned} U &= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} \\ &= Nk_BT \left(\frac{3}{2} + \frac{T}{\xi} \frac{d\xi(T)}{dT}\right) \end{aligned} \tag{10.8}$$

is the sum of two terms: one always equal to $3Nk_BT/2$ which corresponds to the translational degrees of freedom of the gas, and the other which corresponds to the internal degrees of freedom, which is *decoupled* from the other. So the heat capacity of ideal polyatomic gases at constant volume is *different* from that of ideal mono-atomic gases and in general will depend on temperature (but not on $V$). Indeed we have:

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= Nk_B \left(\frac{3}{2} + \left(2 - \frac{T}{\xi}\right)\frac{T}{\xi}\frac{d\xi(T)}{dT} + \frac{T^2}{\xi}\frac{d^2\xi(T)}{dT^2}\right) \end{aligned} \tag{10.9}$$

**Exercise 10.1** Calculate the entropy, $S$, of a polyatomic gas. Does $S \to 0$ when $T \to 0$? Is this behaviour surprising?
**Ans:** $S = Nk_B\left(\ln\left(V/N\right) + 3\ln\left(mk_BT/(2\pi\hbar^2)\right)/2 + 5/2 + \ln\left(\xi\right) + T/\xi \, d\xi/dT\right)$. $S$ does not go to zero when $T$ does, because the classical gas approximation fails at low temperature, where quantum effects become important. ∎

## 10.2   Freezing of internal degrees of freedom

Before we start explicitly calculating $\mathcal{H}_{\text{int}}$ terms, let us look at the low $T$ behaviour of the contribution of the internal degrees of freedom to the gas properties.

In order to do this, we call $\epsilon_0$ the lowest level of all the $\epsilon_\tau$ possible energy levels (i.e. $\epsilon_0$ is the fundamental level of internal structure), $\epsilon_1$ the level just above it (i.e. $\epsilon_1$ is the first excited level of internal structure), and define $g_0$ as the degree of degeneracy of $\epsilon_0$ (i.e. $g_0$ is the number of independent quantum states with the same energy $\epsilon_0$). If $T$ is sufficiently low, i.e. $k_B T \ll \epsilon_1 - \epsilon_0$, all the terms in $\xi(\beta) = \sum_\tau \exp(-\beta\epsilon_\tau)$ are negligible in front of the $g_0$ first ones with energy $\epsilon_0$, so that the internal structure single-particle partition function becomes $\xi(\beta) \simeq g_0 \exp(-\beta\epsilon_0)$, and its logarithm $\ln\xi \simeq -\beta\epsilon_0 + \ln g_0$. This means that at low $T$, all molecules are in the fundamental level of internal structure and as a consequence, all the properties of the polyatomic ideal gas reduce, by and large, to those of a mono-atomic ideal gas. The internal energy, $U$, is simply offset by a constant $N\epsilon_0$, but the heat capacity at constant volume, $C_V$ is the same.

When this happens, one says that the internal degrees of freedom are *frozen* (or *blocked*). It is a pure quantum phenomenon, where the excitation of an internal mode is only possible if $k_B T$ is comparable or greater to the minimal excitation energy of that mode. By contrast, in a classical gas, *any* excitation energy is permitted.

## 10.3   Internal structure of polyatomic molecules

To a good approximation, the internal structure Hamiltonian is the sum of three independent terms:

$$\mathcal{H}_{\text{int}} = \mathcal{H}_e + \mathcal{H}_v + \mathcal{H}_r \tag{10.10}$$

where $\mathcal{H}_e$ is the Hamiltonian of the electrons of the molecule, $\mathcal{H}_v$ describes the vibrations of its atoms with respect to one another and $\mathcal{H}_r$ its rotational motion in space.

> (R)   We should add to this list a 4th term which describes the internal structure of the nuclei of the atoms which compose the molecule. However, the excitation energy of these nuclei are on the order of the MeV (or equivalently $T \sim 10^{10}$K). So the degrees of freedom associated with the nuclei are frozen and we neglect them in what follows.

### 10.3.1   $\mathcal{H}_e$

Even individual atoms possess an internal structure associated with discrete energy levels. However, the excitation energies of $e^-$ in atoms and molecules are of the order of as few eV, i.e. several 10,000 K. So it is only at very high temperatures that the internal structure of atoms may play a role. Until the temperature reaches a few 1000 K, the degrees of freedom associated with $e^-$ are frozen, so they are generally ignored.

> (R)   • Exceptions exist, like the *fine structure* of the fundamental level of atoms and molecules. Remember the paramagnet lecture, and consider an atom/molecule with $\vec{L}$ and $\vec{S}$, the total orbital angular momentum and total spin of its $e^-$ respectively, which both have *non-nil* values in the fundamental state. This is not common, but if it occurs the fundamental level is split into fine structure sub-levels due to the coupling between $\vec{L}$ and $\vec{S}$. The number of these sub-levels is equal to the number of different possible values for the total angular momentum $\vec{J}$: $j = l+s, l+s-1, \cdots, |l-s|$. The energy difference between these sub-levels generally are around a few $10^{-2}$ eV, i.e. $T_e \sim$ a few 100 K, so when the temperature of the thermostat is of that order, one has to account for the fine structure when calculating $\mathcal{Z}_1$ (e.g. for the molecule N-O with

0.015 eV or $T_e \simeq 175$ K). If $T \gg T_e$, one can consider all the fine structure sub-levels as degenerate, and so the $e^-$ degrees of freedom are frozen but with degeneracy factor $g_0 = (2l + 1)(2s + 1)$.

• Finally, note that the fundamental level of atoms/molecules can also have a *hyperfine structure* due to the coupling between nuclei spin and the angular momentum of $e^-$. However the differences in energy between hyperfine levels ($6 \times 10^{-6}$ eV or equivalently $7 \times 10^{-2}$ K for the Hydrogen atom, and higher for other atoms but never above 1.5 K). One therefore "neglects" hyperfine structure and considers all hyperfine sub-levels as degenerate. For atoms with nuclei spin $s_n$, $\mathcal{Z}_1$ is multiplied by $(2s_n + 1)$, and for molecules by $(2s_{n_i} + 1)$ where $n_i$, with $i \in \mathbb{Z}^+$ are the nuclei of the atoms which compose the molecule.

### 10.3.2 $\mathcal{H}_v$

#### – Vibration of a diatomic molecule

Let us first consider a molecule composed of only two atoms. To study its structure we will use what is known as the *Born-Oppenheimer approximation*: we will assume that its nuclei, much more massive than the $e^-$ are separated by a fixed distance, $r$. We then calculate the lowest energy value for the $e^-$ corresponding to this spacing $r$ between nuclei using Quantum Mechanics.

The energy of the system composed of the two nuclei and the $e^-$ is a function $u(r)$ of the distance $r$, which, if the atoms can form a stable molecule, will possess a deep enough minimum for bound states to exist (see Fig. 10.1). The equilibrium distance, $d$, between
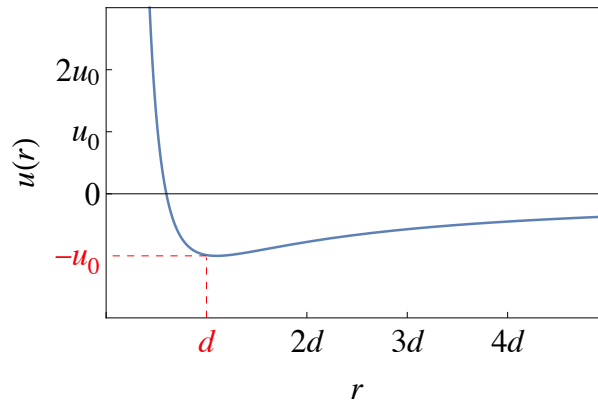


Figure 10.1: Potential energy of a diatomic molecule as a function of the distance $r$, between the two nuclei. Note the electrostatic repulsion (sharp rise) at short distances.

the two nuclei corresponds to this minimum, as indicated on the figure. However, the nuclei can vibrate with respect to one another, so their separation distance $r$ oscillates around $d$. This vibration is equivalent to the motion of a fictitious particle with reduced mass $m_r = m_1 m_2 / (m_1 + m_2)$, where $m_1$ and $m_2$ are the masses of the two nuclei, in the potential drawn on Fig 10.1.

In the limit of small oscillations (or if you prefer in the limit of small extensions to the quantum wave function), from the lecture on the solid crystal, we recognize a one-dimensional harmonic oscillator with angular frequency $\omega = \sqrt{\kappa/m_r}$ where $\kappa$ is the curvature of $u(r)$ at its minimum $u_0$, i.e. for the equilibrium distance $d$. So the vibration

energy levels from the minimum $u_0$ are given by

$$\epsilon_n = \left( n + \frac{1}{2} \right) \hbar\omega \quad \text{with} \ \ n \in \mathbb{Z}^+ \tag{10.11}$$

and the level $\epsilon_n$ is *non-degenerate*, i.e. it corresponds to a unique quantum state of vibration. In this case, the single-particle partition function writes:

$$\xi_v(\beta) = \sum_{n=0}^{+\infty} \exp\left( - \beta(n+1/2)\hbar\omega \right) \tag{10.12}$$

and the associated internal energy:

$$U_v = -N\frac{\mathrm{d}\ln\xi_v}{\mathrm{d}\beta} = N\hbar\omega \left( \frac{1}{2} + \frac{1}{\exp(\beta\hbar\omega) - 1} \right) \tag{10.13}$$

The extra heat capacity of the gas due to molecule vibration thus reads:

$$C_V^{(v)} = Nk_B \frac{\left(\hbar\omega/(2k_BT)\right)^2}{\sinh^2\left(\hbar\omega/(2k_BT)\right)} = Nk_B \frac{\left(T_v/(2T)\right)^2}{\sinh^2\left(T_v/(2T)\right)} \tag{10.14}$$

where we have defined the *characteristic vibrational temperature* as $T_v \equiv \hbar\omega/k_B$. We can
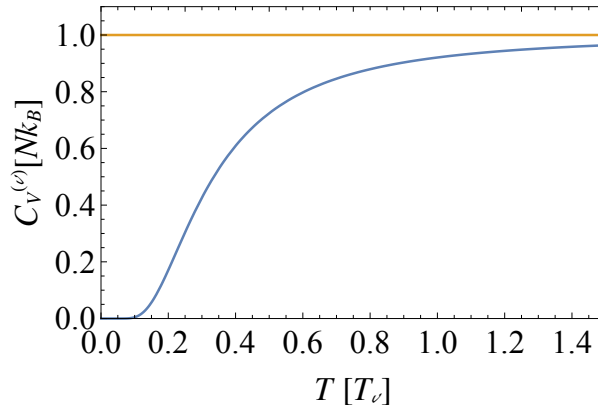


Figure 10.2: Heat capacity of a diatomic molecule due to vibration, as a function of temperature.

see that for $T \ll T_v$, we have $C_V^{(v)} \to 0$ like $Nk_B(T_v/T)^2 \exp(-T_v/T)$. On the other hand, for $T \gg T_v$, $C_V^{(v)} \simeq Nk_B$, i.e. is independent of temperature, in line with the classical theorem of equipartition of energy applied to the one dimensional harmonic oscillator. These considerations lead to the diagram 10.2.

(R)    $T_v$ increases when the inter-atomic forces increase, but varies between a few hundred
       K (463 K for the molecule $Br_2$) to a few 1000 K (6215 K for $H_2$).

**– Vibration of a polyatomic molecule**

If the molecules are composed of $q \in \{3, 4, \cdots, +\infty\}$ atoms, the number of degrees of freedom for vibrations $q_v$, i.e. the number of variables necessary to characterise the relative positions of their $q$ nuclei, is $q_v = 3q - 6$. Indeed, one has to account for the positions of all nuclei of the molecule and remove the coordinates of its centre of mass (3 degrees of freedom corresponding to the translational motion), along with the 3 Euler angles[¶] necessary to describe the orientation of the molecule in space (associated with the degrees of freedom of rotational motion as we will see later on).

The potential energy $u(r)$ becomes $u(r_i)$ where the index $i \in \{q_v\}$ and the nuclei are located at equilibrium distances $d_i$. We are thus dealing with a system of $q_v$ coupled harmonic oscillators, which can be shown to be equivalent to a fictitious system of $q_v$ one-dimensional independent harmonic oscillators. So the generalisation from the diatomic molecule heat capacity to that of the polyatomic molecule is quite straightforward:

$$C_V^{(v)} = N k_B \sum_{i=1}^{q_v} \frac{\left(T_{v,i}/(2T)\right)^2}{\sinh^2\left(T_{v,i}/(2T)\right)} \tag{10.15}$$

where $T_{v,i} \equiv \hbar \omega_i / k_B$ represents the different characteristic vibrational temperatures of the polyatomic molecule.

### 10.3.3 $\mathcal{H}_r$

Molecules also possess rotational excitation modes which correspond to their rotational kinetic energy in three-dimensional space. We will assume in what follows that distances between nuclei remain constant during the rotation of the molecule, i.e. the molecule behaves as a *rigid rotator*[∥].

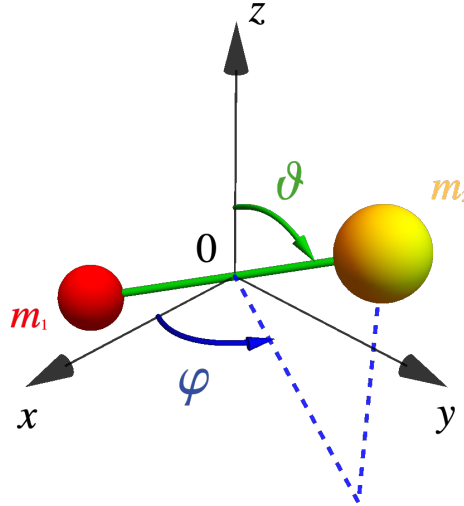**– Rotation of a diatomic molecule**



Figure 10.3: Schematic diagram of a diatomic molecule showing its orientation in three-dimensional space. The origin of the coordinate system is located at the centre of mass of the molecule. Distances $r_1$ and $r_2$ separate the origin from the nuclei of the molecule's atoms. The distance $d = r_1 + r_2$ separating the two nuclei is the length of the green rod.

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[¶] Unless the molecule is linear, in which case 2 Euler angles are enough and $q_v = 3q - 5$ in this case.
[∥] In other words we neglect the centrifugal force felt by the nuclei during rotation.

As is clear from the diagram 10.3, the position of the centre of mass of the molecule is already accounted for in the degrees of freedom associated with the translational motion of the molecule, so its orientation in space is simply given by two Euler angles $\vartheta$ and $\varphi$.

The rotational kinetic energy of such a molecule, is, according to your Classical Mechanics lectures,

$$\epsilon_r = \frac{\mathcal{I}}{2}\left(\left(\frac{\mathrm{d}\vartheta}{\mathrm{d}t}\right)^2 + \left(\frac{\mathrm{d}\varphi}{\mathrm{d}t}\right)^2\sin^2\vartheta\right) = \frac{\vec{L}^2}{2\mathcal{I}} \tag{10.16}$$

where $\vec{L}$ is the angular momentum of the molecule and $\mathcal{I}$ the moment of inertia with respect to its centre of mass, i.e. w.r.t. any axis going through the centre of mass and perpendicular to the molecule axis. For a diatomic molecule, we have** $\mathcal{I} = m_r\, d^2$, keeping the notation for the reduced mass $m_r$ and equilibrium separation $d$ that we introduced for these molecules in the lecture on vibrations.

So the Quantum Mechanics Hamiltonian associated to the rotation of such linear molecules is:

$$\mathcal{H}_r = \frac{\vec{\mathcal{L}}^2}{2\mathcal{I}} \tag{10.17}$$

where $\vec{\mathcal{L}}$ is the *orbital* angular momentum operator. From your Quantum Mechanics lectures, you know the stationary states of rotation. The corresponding wave functions are the so-called spherical harmonics $\mathcal{Y}_l^m(\vartheta,\varphi)$, where $l \in \mathbb{Z}^+$ and $m \in \{-l, \cdots, l\}$. The energy levels associated to these states depend only on $l$, *not* on $m$, i.e. these levels are $2l+1$ degenerate:

$$\epsilon_{l,m} = \frac{\hbar^2}{2\mathcal{I}}l(l+1) \tag{10.18}$$

and following what we did for vibrations, we introduce a *characteristic rotational temperature* $T_r \equiv \hbar^2/(2\mathcal{I}k_B)$.

(R)   For light molecules with small $\mathcal{I}$, $T_r$ can be quite high (85 K for $H_2$). However for the vast majority of molecules $T_r$ is much lower, around a few K. So except for molecular hydrogen, one is practically always in the case where $T \gg T_r$, and the rotational degrees of freedom of the molecule are *not* frozen and can be treated classically (i.e. considered as continuous).

Let us consider a molecule made of two *different* atoms, like HCl. Its single-particle partition function is:

$$\begin{aligned}
\xi_r(\beta) &= \sum_{l=0}^{+\infty}\sum_{m=-l}^{+l}\exp(-\beta\epsilon_{l,m})\\
&= \sum_{l=0}^{+\infty}(2l+1)\exp\left(-\beta\frac{\hbar^2}{2\mathcal{I}}l(l+1)\right)\\
&= 1 + 3\exp(-2\,T_r/T) + 5\exp(-6\,T_r/T) + 7\exp(-12\,T_r/T) + \cdots \tag{10.19}
\end{aligned}$$

There is no simple method to evaluate this infinite sum exactly, however two important remarks can be made. First, in the infrequent case where $T \leq T_r$, one should remember

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**Note that we neglect any rotation around the molecule axis because the moment of inertia in that case would be due to the $e^-$ instead of the nuclei and therefore about 2000 times smaller given the mass difference.

that the terms of the sum decay rapidly, so that a good approximation can be obtained by considering only the first few ones and neglecting the rest. Second, in the most likely case where $T \gg T_r$, two consecutive terms are "close enough" to allow us to approximate the discrete sum over $l$ by a continuous integral, thus writing:

$$\xi_r(\beta) \simeq \int_{l=0}^{+\infty} (2l+1) \exp\left(-\beta \frac{\hbar^2}{2\mathcal{I}} l(l+1)\right) \mathrm{d}l \tag{10.20}$$

which, after the change of variable $y = l(l+1)$ yields

$$\xi_r(T) \simeq \frac{T}{T_r} \tag{10.21}$$

The associated internal energy for $T \gg T_r$ thus reads:

$$U_r = -N \frac{\mathrm{d}\ln\xi_r}{\mathrm{d}\beta} = N k_B T \tag{10.22}$$

as expected from the classical equipartition of energy theorem since we have summed two quadratic terms (in the kinetic energy of rotation of the molecule, see equation (10.16)). In this high temperature regime, the extra heat capacity of the gas due to molecule rotation is thus simply:

$$C_V^{(r)} = N k_B \tag{10.23}$$

> **Exercise 10.2** Estimate $C_V^{(r)}$ in the low temperature regime ($T \leq T_r$) by assuming that all the other terms in the sum (10.19) are negligible in front of the first two. What is the limit of $C_V^{(r)}$ when $T \to 0$?
> **Ans:** $C_V^{(r)} = 12 k_B (T_r/T)^2 \exp(-2T_r/T)/\left(1 + 3\exp(-2T_r/T)\right)^2$, so $\lim_{T \to 0} C_V^{(r)} = 0$. ∎

Numerically evaluating the sum (10.19) (and given the limits at low and high $T$ that we have previously estimated), we arrive to the following graph for the heat capacity of a diatomic molecule:
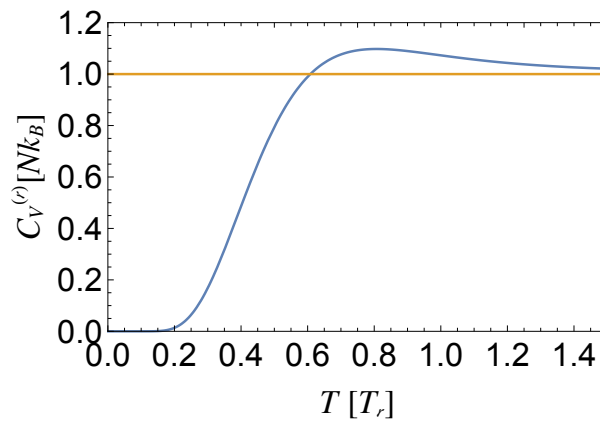


Figure 10.4: Heat capacity of a diatomic molecule due to rotation, as a function of temperature.

What if the two atoms constituting the molecule are *identical*, like $H_2$, $O_2$, $N_2$? In this case, one has to take into account the quantum principle of symmetrisation to count

its states. The only states allowed are those which are symmetrical when the two nuclei are swapped if these nuclei are bosons with integer spin, or anti-symmetrical if the nuclei are fermions with half-integer spin. You can see that that while the translational motions can safely ignore this constraint as they deal with the motion of the centre of mass of the molecule and not the relative position of the two nuclei[††], this is not the case for rotations which can swap nuclei positions (e.g. $\vartheta \to \pi - \vartheta$ and $\varphi \to \pi + \varphi$). One can show that (left as an exercise), in that case, whether for bosons or fermions, if $T \gg T_r$, the single-particle partition function is:

$$\xi_r(T) \simeq (2s_n + 1)^2 \frac{T}{2T_r} \tag{10.24}$$

where $s_n$ is the nuclear spin. Therefore both $U_r$ and $C_V^{(r)}$ are the same as for a molecule with two different atoms.

**– Rotation of a polyatomic molecule**

What about if the molecule is composed of more atoms than just two? Well, we have to distinguish between two cases. First, and most simple, is the case where the molecule is *linear*. Then we can develop arguments like those we used for the diatomic molecule, leading to

$$\xi_r(T) \simeq \frac{1}{\sigma} \frac{T}{T_r} \tag{10.25}$$

where $\sigma$ is called the *symmetry factor* and has values of 1 for non-symmetric molecules such as $N_2O$ (N-N-O) or 2 for symmetric molecules such as $CO_2$ (O-C-O)[‡‡]. As a consequence, both $U_r$ and $C_V^{(r)}$ are the same as for a diatomic molecule.

The second case is that of a *non-linear* molecule. It thus possesses three degrees of rotational freedom. Consider that it is rotating like a rigid block so we can apply the classical results of solid kinematics: we have to define three moments of inertia $\mathcal{I}_1$, $\mathcal{I}_2$ and $\mathcal{I}_3$ with respect to its principal axes of inertia. We need three Euler angles to characterise the rotation, and three characteristic rotational temperatures (one per moment of inertia) $T_{r,p} \equiv \hbar^2/(2k_B\mathcal{I}_p)$ with $p \in \{1,2,3\}$. In practice, we almost always have $T \gg T_{r,p}$ and therefore have:

$$\xi_r(T) \simeq \frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T}{T_{r,1}}} \sqrt{\frac{T}{T_{r,2}}} \sqrt{\frac{T}{T_{r,3}}} \tag{10.26}$$

where $\sigma$ is a symmetry factor exactly like in the case of a linear molecule, except its values are not limited to 1 or 2. For instance, the benzene molecule, $C_6H_6$ has $\sigma = 12$. More importantly however, this leads to $U_r = 3Nk_BT/2$ and $C_V^{(r)} = 3Nk_B/2$ in the high temperature regime, again in agreement with the classical theorem of equipartition of energy.

### 10.3.4 Putting $C_V$ all together

As translational, rotational and vibrational motions are considered *independent* of one another, the total heat capacity at constant volume of the molecular gas, $C_V$ is simply the

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[††]The same is true for vibrations which only depend on the distance $r$ between nuclei and are therefore invariant upon the permutation of these latter.

[‡‡]You can understand this intuitively: if the molecule is symmetric, you do not change the single-particle partition function by swapping the symmetric nuclei, so you have to divide the total number of states by 2.
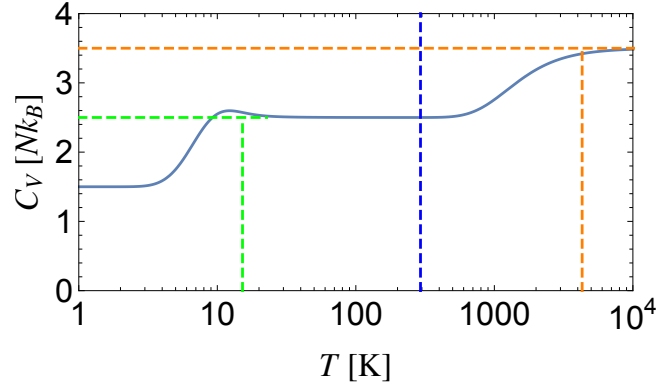
Figure 10.5: Total heat capacity of the HCl diatomic molecule ($T_r = 15.2$K and $T_v = 4303$K indicated by vertical green and orange dashed lines respectively) due to translational, rotational and vibrational motions, as a function of temperature. The blue vertical dashed line represents a typical lab temperature of 293K, and is given for reference.

sum of all the contributions. This yields in the high temperature regime ($T \gg T_{r,p}$):

$$
\begin{aligned}
C_V &= C_V^{(t)} + C_V^{(r)} + C_V^{(v)} && (10.27) \\
&= \frac{3}{2}Nk_B + \left\{ \begin{array}{ll} Nk_B & \text{(linear molecule)} \\ \frac{3}{2}Nk_B & \text{(non}-\text{linear molecule)} \end{array} \right. + Nk_B \sum_{i=1}^{q_v} \frac{\left(T_{v,i}/(2T)\right)^2}{\sinh^2\left(T_{v,i}/(2T)\right)}
\end{aligned}
$$

where the different characteristic vibrational temperatures, $T_{v,i}$ are associated with the different vibrational modes which will be excited in turn as $T$ increases. So some of them will be in the classical limit while others are still frozen! Finally, for a diatomic molecule, this sum of terms simplifies to $Nk_B\left(T_v/(2T)\right)^2/\sinh^2\left(T_v/(2T)\right)$ and contributes accordingly to the total $C_V$ plotted in Fig. 10.5.