

## Chapter 10

# Gases in the classical limit

At the end of chapter 6 we came up with a definition of the classical limit in terms of the ratio of the inter-particle separation to the de Broglie wavelength. If the particles in the gas are sufficiently dilute that their wave-packets don't overlap, there will be no competition for states and so the quantum occupation rules have no relevance.

In terms of the  $g$ 's and  $n$ 's of chapter 6, what does this imply? Let's define the energy range  $\mathcal{E} \rightarrow \mathcal{E} + d\mathcal{E}$  as a discrete energy  $\mathcal{E}_i$  with degeneracy  $g_i = g(\mathcal{E}_i) d\mathcal{E}$ . What can we deduce about a typical  $g_i$  and  $n_i$ ? We'll take the example of nitrogen, whose molecules have a mass of  $5.2 \times 10^4 m_e$ . At standard temperature and pressure (STP),  $N/V = 2.7 \times 10^{25} \text{ m}^{-3}$ . You should be able to look back at the numbers for chapter 6 and convince yourself that this is well into the classical limit.

Now set  $\Delta\mathcal{E} = k_B T / 10^{10}$  and put in the numbers, and you'll see that for energies near room temperature,  $g_i \sim 10^{20}$  and  $n_i \sim 10^{14-15}$ . In this estimate, we come to our  $n_i$  by dividing the particles up roughly equally between all the levels available to them below  $k_B T$ , but the details are not important. We do it just to re-emphasise something that we mentioned before: **for a gas in the classical limit**

$$g_i \gg n_i \gg 1 .$$

How does this change the counting rules that we set up for the quantum gases in chapter 6? Well, let's look at the case for bosons. Recall equation 6.2:

$$\Omega_b = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad (6.2)$$

Now, it should be easy to see that  $(x - 1)! = x!/x$ , and if we apply this to  $(n_i + g_i - 1)!$  in the numerator, and also apply it to  $(g_i - 1)!$  in the denominator, then

$$\Omega_b = \prod_i \frac{(n_i + g_i)! g_i}{(n_i + g_i) n_i! g_i!} \quad (10.1)$$

Given that we are in the regime where  $g_i \gg n_i$ , then we can say that  $g_i/(n_i + g_i) \approx 1$ , so

$$\begin{aligned}\Omega_b &\approx \prod_i \frac{(n_i + g_i)!}{n_i! g_i!} \\ &= \prod_i \frac{1}{n_i! g_i!} (n_i + g_i) \times (n_i + g_i - 1) \times (n_i + g_i - 2) \dots \times (g_i + 1) \times g_i \times (g_i - 1) \dots \times 2 \times 1\end{aligned}\quad (10.2)$$

Consider the product  $(n_i + g_i) \times (n_i + g_i - 1) \times (n_i + g_i - 2) \dots \times (g_i + 1)$ : this multiplies together  $n_i$  terms involving  $g_i$ , so will yield  $g_i^{n_i}$  plus a shed-load of cross terms involving *lower* powers of  $g_i$ . Given  $g_i \gg n_i \gg 1$ , then we can ignore these cross terms, and the term inside the product sign becomes  $g_i^{n_i} g_i! / n_i! g_i!$ . The  $g_i!$  terms cancel and we end up with

$$\Omega = \prod_i \frac{g_i^{n_i}}{n_i!} \quad (10.3)$$

Unsurprisingly, the expression for fermions (6.3) can be reduced to identical form, which is why we have dropped the  $b$  subscript in equation 10.3. This limiting case is called the Maxwell-Boltzmann case, so we can restate the above expression as

$$\Omega_{\text{MB}} = \prod_i \frac{g_i^{n_i}}{n_i!} \quad (10.4)$$

## 10.1 The Maxwell-Boltzmann distribution

Once again, we seek to maximise  $\Omega$ , and end up with three constraint equations:

$$d \ln \Omega = \sum_i \ln \left( \frac{g_i}{n_i} \right) dn_i = 0 \quad \sum_i dn_i = 0 \quad \sum_i \mathcal{E}_i dn_i = 0 \quad (10.5)$$

We get

$$\frac{n_i}{g_i} = f_{\text{MB}} = \frac{1}{e^{-\alpha + \beta \mathcal{E}_i}} \quad (10.6)$$

which is the *Maxwell-Boltzmann distribution*. (If you look back to equation 6.13, you'll see that we actually reached the same conclusion there by considering what happened when the degeneracy got very large. We have just reached it here in a slightly more rigorous manner.)

## 10.2 The entropy of a classical-limit gas

Equation 10.6 can be re-arranged to

$$n_i = A g_i e^{-\mathcal{E}_i / k_B T} \quad (10.7)$$

This is just the Boltzmann distribution again, so why did we bother working out this distribution? Well, let's look at the entropy  $S = k_B \ln \Omega$ , so

$$\begin{aligned} S &= k_B \left( \sum_i n_i \ln g_i - n_i \ln n_i + n_i \right) \\ &= k_B \left( \sum_i n_i \ln \left( \frac{g_i}{n_i} \right) + \sum_i n_i \right) \\ &= k_B \left( \sum_i n_i \ln \left( \frac{g_i}{n_i} \right) + N \right) \end{aligned} \quad (10.8)$$

$$(10.9)$$

Using equation 10.7, we can see that

$$\ln \left( \frac{g_i}{n_i} \right) = \ln g_i - \ln A - \ln g_i + \frac{\mathcal{E}_i}{k_B T} \quad (10.10)$$

so

$$S = k_B \left( -N \ln A + \frac{U}{k_B T} + N \right) \quad (10.11)$$

Equation 10.7 tells us  $n_i$ , and we know that  $N = \sum_i n_i$ , so  $N = A \sum_i g_i e^{-\mathcal{E}_i/k_B T}$ . However, remember that  $Z_{\text{sp}} = \sum_i g_i e^{-\mathcal{E}_i/k_B T}$ , so  $N = A Z_{\text{sp}}$ . Thus,

$$\ln A = \ln N - \ln Z_{\text{sp}} \quad (10.12)$$

We can insert this expression for  $\ln A$  into (10.11) to give

$$\begin{aligned} S &= k_B \left( -N \ln N + N \ln Z_{\text{sp}} + \frac{U}{k_B T} + N \right) \\ &= k_B \left( N \ln Z_{\text{sp}} + \frac{U}{k_B T} - \ln N! \right) \end{aligned} \quad (10.13)$$

We can compare this with equation 4.40 ( $S = N k_B \ln Z_{\text{sp}} + \frac{U}{T}$ ) and see that the entropy is not quite the same as it was for Boltzmann statistics and distinguishable particles, it is *less* by  $k_B \ln N!$ . This is not so surprising, once you think about it: there must be fewer ways of arranging indistinguishable particles than distinguishable ones (hence a lower  $S$ ), even in the classical limit.

### 10.3 $Z_{\text{sp}}$ for a classical-limit gas

Our next task is to calculate the single-particle partition function for the ideal monatomic gas. It is definitely most convenient to re-adopt the continuum approximation:

$$\begin{aligned} Z_{\text{sp}} &= \int_0^\infty g(\mathcal{E}) e^{-\mathcal{E}/k_B T} d\mathcal{E} \\ &= \int_0^\infty \frac{V m^{3/2}}{\sqrt{2} \pi^2 \hbar^3} \mathcal{E}^{1/2} e^{-\mathcal{E}/k_B T} d\mathcal{E} \end{aligned}$$

At this stage, it is actually easier to revert to the density of  $k$ -states and integrate with respect to  $dk$ . Remember,  $g(k) dk = g(\mathcal{E}) d\mathcal{E}$ , so provided we use the density of states in the form (6.19) and use the correct relation to substitute for  $\mathcal{E}$  in terms of  $k$  (6.21), we get

$$Z_{\text{sp}} = \frac{V}{2\pi^2} \int_0^\infty k^2 \exp\left(-\frac{\hbar^2 k^2}{2mk_B T}\right) dk \quad (10.14)$$

(Convince yourself that the  $\mathcal{E} - k$  relation we used when deriving the density of states means that both the expression we are integrating and the limits make sense.)

We use the standard integral

$$\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{a^3}} \quad (10.15)$$

with  $a = \hbar^2/2mk_B T$  and we get

$$Z_{\text{sp}} = V \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \quad (10.16)$$

As it stands, this result is only valid for a *monatomic* gas because it does not include any internal motions or *degrees of freedom* of the constituent gas ‘particles’.

## 10.4 The Maxwell-Boltzmann distribution of speeds

Just as we arrived at infinitesimal expressions for the Bose Einstein and Fermi-Dirac distributions by replacing  $n_i$  and  $g_i$  with  $n(\mathcal{E}) d\mathcal{E}$  and  $g(\mathcal{E}) d\mathcal{E}$ , we can express the Maxwell-Boltzmann distribution (equation 10.7) as

$$n(\mathcal{E}) d\mathcal{E} = g(\mathcal{E}) d\mathcal{E} A \exp(-\mathcal{E}/k_B T) \quad (10.17)$$

If we are interested in what the distribution looks like as a function of the *velocities* of the particles, we simply write  $\mathcal{E}$  as  $\mathcal{E}(v)$  to obtain

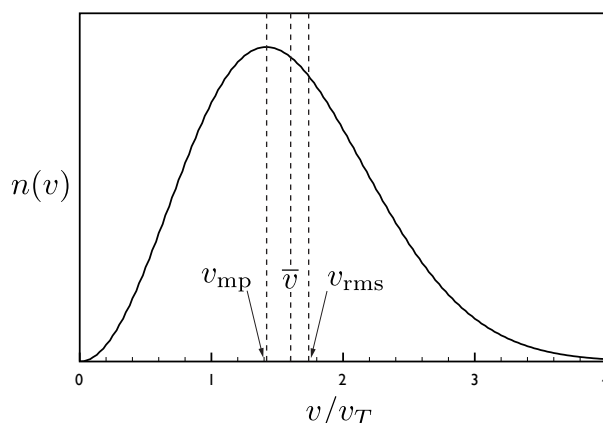
$$n(v) dv = g(v) dv A \exp(-\mathcal{E}(v)/k_B T) \quad (10.18)$$

Now  $g(\mathcal{E}) d\mathcal{E} = g(v) dv = g(k) dk$ , which we have already worked out as equation 6.19. The linear momentum of a particle is  $\hbar k = mv$ , so we can express  $k^2$  and  $dk$  in terms of  $v$ . Noting that the energy is simply  $mv^2/2$ , and  $A = N/Z$ , we can show that

$$n(v) dv = N \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv \quad (10.19)$$

The distribution of speeds is shown in figure 10.1, as a function of  $v/v_T$ , where  $v_T = \sqrt{k_B T/m}$ , i.e the speed of a particle with kinetic energy  $k_B T$ .

Three velocities of particular interest are indicated in figure 10.1.  $v_{\text{mp}} = \sqrt{2} v_T$  is the *most probable* speed, corresponding to the peak of the curve.  $\bar{v} = \sqrt{8/\pi} v_T$  is the *mean* speed of the particles and  $v_{\text{rms}} = \sqrt{3} v_T$  is the *root mean square* speed.



**Figure 10.1:** The distribution of speeds in a gas obeying Maxwell-Boltzmann statistics.  $v_T$  is defined as  $\sqrt{k_B T/m}$ .  $v_{mp}$  is the most probable speed,  $\bar{v}$  is the mean speed and  $v_{rms}$  is the root-mean-square speed.

The average kinetic energy per particle is

$$\bar{\mathcal{E}} = \frac{1}{2} m v_{rms}^2 = \frac{3}{2} k_B T \quad (10.20)$$

Our system of  $N$  particles, therefore, must have total energy  $U = \frac{3}{2} N k_B T$ .

Earlier we saw that we can also get the energy from the partition function. Using  $Z_N = \frac{Z_{sp}^N}{N!}$  and  $U = k_B T^2 \frac{\partial(\ln Z_N)}{\partial T}$ , we find that  $\frac{\partial(\ln Z_N)}{\partial T} = \frac{3}{2} \frac{N}{T}$  and so we again get to  $U = \frac{3}{2} N k_B T$ .

## 10.5 Partition functions of entire systems

Implicit in all the results that we derived and discussed in chapters 4 and 6 was the fact, that we could write the partition function of a system of  $N$  particles as the product of  $N$  single-particle partition functions:

$$Z_N = Z_{sp}^N \quad (10.21)$$

This property originates in the fact that the joint probabilities for  $N$  distinguishable particles was a product over the  $N$  individual occupation probabilities. It also ensured the sensible factor of  $N$  in front of all the observables.

This is, however, related to the condition of distinguishability. So what's the script for *indistinguishable* particles?

Note that we could make the functional form of the entropies of a quantum gas in the classical limit (10.13) and the distinguishable Boltzmann gas (4.40) identical, if we defined the partition function for the whole system (the 'classical limit' partition function) as

$$Z_N = \frac{Z_{sp}^N}{N!} \quad (10.22)$$

The subtlety of distinguishability that affects the entropy of an ideal gas does not have any effect on many other observables such as the internal energy (and hence the specific heat) or the Maxwell-Boltzmann distribution of speeds. As has been stressed from the beginning, indistinguishability is a fundamentally quantum mechanical effect, and so was not included in the 19th century statistical mechanics of, for example, Boltzmann and Maxwell.

Gibbs, however, noticed that if you used distinguishable statistical physics to look at the entropy of mixing of gases, all was not well... His **Gibbs paradox** was one of the earliest (and faintest!) manifestations of the need for quantum mechanics, and thus has a real place in the history of physics.

## 10.6 Ideal gases consisting of molecules

Imagine a molecule like  $N_2$  which is like a ‘flying sprung dumbbell’: as well as simply flying around (like, say, an He atom), it can rotate and vibrate about its centre of mass. Without going into details, we can see that both the rotational and vibrational motion will be quantised.

Each molecule will have some probability of being in a certain translational state, combined with some other probability of being in a given rotational state and a third probability of being in a certain vibrational state. Assuming that the motions are all independent, the total probability will be the product of the three, the total energy the sum of the three eigenvalues and the total partition function the product of the individual ones:

$$\mathcal{E}_{\text{tot}} = \mathcal{E}_{\text{trans}} + \mathcal{E}_{\text{rot}} + \mathcal{E}_{\text{vib}} \quad (10.23)$$

$$Z_N^{\text{tot}} = Z_N^{\text{trans}} \times Z_N^{\text{rot}} \times Z_N^{\text{vib}} \quad (10.24)$$

For a description of this molecular physics, see Glazer & Wark, chapter 5.

## 10.7 The Gibbs paradox of the classical statistical mechanics of distinguishable particles

We mentioned the Gibbs paradox briefly above, and let’s look at it in more detail now. Recall the form of two of the thermodynamic properties that we derived in section 4 for our crystal of distinguishable particles: the internal energy and the entropy:

$$U = k_B T^2 N \frac{\partial (\ln Z_{\text{sp}})}{\partial T} \quad (4.38)$$

$$S = N k_B \ln Z_{\text{sp}} + \frac{U}{T} \quad (4.40)$$

$$= N k_B \left( \ln Z_{\text{sp}} + T \frac{\partial (\ln Z_{\text{sp}})}{\partial T} \right) \quad (10.25)$$

It can be seen from (10.25) that for our crystal of distinguishable atoms,  $S$ , like other thermodynamic observables, scales with  $N$ : this is quite sensible as in a crystal  $N$  is proportional to the volume, so

it means that  $S$  also scales as the volume. This is a property demanded by thermodynamics and is known as *extensivity*.

What happens in a classical Boltzmann gas of distinguishable particles? Well, again we use equation 10.25, i.e. we use the expression resulting from the assumption that

$$Z_N = Z_{\text{sp}}^N$$

which is valid for distinguishable particles. For an ideal gas, we use equation 10.16

$$Z_{\text{sp}} = V \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \quad (10.16)$$

the derivation of which *made no assumptions about (in)distinguishability*. Returning to equation 10.25 and now using equation 10.16 for  $Z_{\text{sp}}$ , the first term inside the bracket of (10.25) is

$$\ln Z_{\text{sp}} = \ln \left[ V \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \right] = \ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln \left( \frac{mk_B}{2\pi\hbar^2} \right) \quad (10.26)$$

and the second term inside the bracket of (4.40) is

$$T \frac{\partial(\ln Z_{\text{sp}})}{\partial T} = \frac{3}{2} \quad (10.27)$$

(which you can prove to yourself). Thus

$$S = Nk_B \left[ \ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln \left( \frac{mk_B}{2\pi\hbar^2} \right) + \frac{3}{2} \right] \quad (10.28)$$

What happens now if we double  $N$  at constant temperature  $T$  and at constant density  $N/V$ ? Well,  $V$  must also double, which means that the  $\ln V$  term inside the square bracket will increase. The effect of this is that  $S$  *more than doubles*. This means that Boltzmann statistical mechanics applied to ideal gases *is not consistent with the laws of thermodynamics!* (Oops...) This was **Gibbs' paradox**.

Let's now define the particles in our gas as *fundamentally indistinguishable*. This means that we need to use a different expression for the entropy to equation 4.40, as that was for distinguishable particles. Luckily, we derived such an expression in equation 10.13:

$$S = k_B \left( N \ln Z_{\text{sp}} + \frac{U}{k_B T} - \ln N! \right) \quad (10.13)$$

$$= Nk_B \left( \ln Z_{\text{sp}} + T \frac{\partial(\ln Z_{\text{sp}})}{\partial T} - \frac{\ln N!}{N} \right) \quad (\text{convince yourself...})$$

$$= Nk_B \left[ \ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln \left( \frac{mk_B}{2\pi\hbar^2} \right) - \ln N + \frac{5}{2} \right]$$

$$= Nk_B \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln T + \frac{3}{2} \ln \left( \frac{mk_B}{2\pi\hbar^2} \right) + \frac{5}{2} \right] \quad (10.29)$$

If we double  $N$  while keeping  $(N/V)$  constant, then the content of the square bracket is unchanged, so  $S$  is extensive again.

'Classical' statistical mechanics of the ideal gas only obeys the laws of thermodynamics if the particles are fundamentally indistinguishable. This is the reason why we have consistently used the rather clumsy 'classical-limit quantum gas' rather than the much easier 'classical gas' as the point is that in a 'fully' classical gas, the particles are distinguishable as we could in principle follow their trajectories around.

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