25 Relativistic gases

In this chapter we will repeat our derivation of the partition function for a gas, and hence of the other thermodynamic properties which can be obtained from it, but this time include relativistic effects. We will see that this leads to some subtle changes in these properties which have profound consequences. First we will review the full relativistic dispersion relation for particles with non-zero mass and then derive the partition function for ultrarelativistic particles.

25.1 Relativistic dispersion relation for massive particles

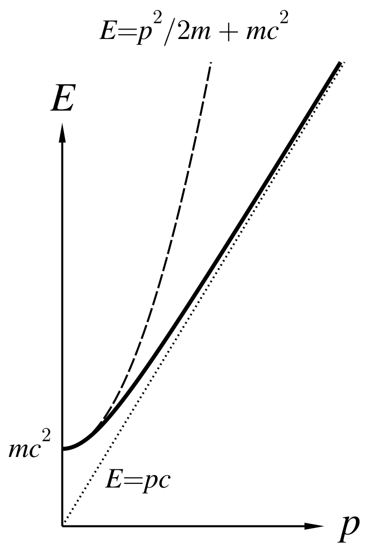

Fig. 25.1 The dispersion relation of a particle with mass (thick solid line) according to eqn 25.1. The dashed line is the non-relativistic limit ($p \ll mc$). The dotted line is the ultrarelativistic limit ($p \gg mc$).

In deriving the partition function for a gas, we assumed that the kinetic energy E of a molecule of mass m was equal to $p^2/2m$, where p is the momentum (and using $p = \hbar k$, we wrote down $E(k) = \hbar^2 k^2/2m$; see eqn 21.15). This is a classical approximation valid only when $p/m \ll c$ (where c is the speed of light), and in general we should use the relativistic formula

$$E^2 = p^2c^2 + m^2c^4, \tag{25.1}$$

where m is now taken to be the **rest mass**, i.e. the mass of the molecule in its rest frame. This is plotted in Fig. 25.1. When $p \ll mc$ (the **non-relativistic limit**) this reduces to

$$E = \frac{p^2}{2m} + mc^2, \tag{25.2}$$

which is identical to our classical approximation $E = p^2/2m$ apart from the extra constant mc^2 (the rest mass energy), which just defines a new 'zero' for the energy (see Fig. 25.1). In the case $p \gg mc$ (the **ultrarelativistic limit**), eqn 25.1 reduces to

$$E = pc, \tag{25.3}$$

which is the appropriate relation[1] for photons (this is the straight line in Fig. 25.1).

[1] The relation between E and p is known as a **dispersion relation**. By scaling $E = \hbar\omega$ and $p = \hbar k$ by a factor $\hbar$ we have a relation between ω and k, which is perhaps more familiar as a dispersion relation from wave physics.

25.2 The ultrarelativistic gas

Let us now consider a gas of particles with non-zero mass in the ultrarelativistic limit which means that $E = pc$. Such a linear dispersion relation means that some of the algebra in this chapter is actually much simpler than we had to deal with for the partition function in the non-relativistic case where the dispersion relation is quadratic. Using the ultrarelativistic limit means that all the particles (or at the very least, the vast majority of them), will be moving so quickly that their kinetic energy is much greater than their rest mass energy.[2] Using the ultra-relativstic limit $E = pc = \hbar kc$, we can write down the single-particle partition function

$$Z_1 = \int_0^\infty \mathrm{e}^{-\beta\hbar kc} g(k)\,\mathrm{d}k, \tag{25.4}$$

where we recall that (eqn 21.6)

$$g(k)\,\mathrm{d}k = \frac{Vk^2\,\mathrm{d}k}{2\pi^2}, \tag{25.5}$$

and so, using the substitution $x = \beta\hbar kc$, we have

$$Z_1 = \frac{V}{2\pi^2}\left(\frac{1}{\beta\hbar c}\right)^3 \int_0^\infty \mathrm{e}^{-x} x^2\,\mathrm{d}x, \tag{25.6}$$

and recognizing that the integral is 2!, we have finally that

$$Z_1 = \frac{V}{\pi^2}\left(\frac{k_\mathrm{B}T}{\hbar c}\right)^3. \tag{25.7}$$

Notice immediately that we find that $Z_1 \propto VT^3$, whereas in the non-relativistic case we had that $Z_1 \propto VT^{3/2}$. We can also write eqn 25.7 in a familiar form

$$Z_1 = \frac{V}{\Lambda^3}, \tag{25.8}$$

where Λ is not the same as the expression for the thermal wavelength in eqn 21.18, but is given by

$$\Lambda = \frac{\hbar c \pi^{2/3}}{k_\mathrm{B}T}, \tag{25.9}$$

It now becomes a simple exercise to determine all the properties of the ultrarelativistic gas using our practiced methods of partition functions.

[2]Note however that we are ignoring any quantum effects which may come into play; these will be considered in Chapter 30.

Equivalently, one can write

$$\Lambda = \frac{hc}{2\pi^{1/3}k_\mathrm{B}T},$$

Example 25.1

Find U, C_V, F, p, S, H and G for an ultrarelativistic gas of indistinguishable particles.
Solution:
The N-particle partition function Z_N is given by[3]

$$Z_N = \frac{Z_1^N}{N!}, \tag{25.10}$$

and hence

$$\ln Z_N = N \ln V + 3N \ln T + \text{constants}. \tag{25.11}$$

[3]This is assuming the density is not so high that this approximation breaks down.

The internal energy U is given by

$$U = -\frac{\mathrm{d}\ln Z_N}{\mathrm{d}\beta} = 3Nk_\mathrm{B}T, \tag{25.12}$$

which is different from the non-relativistic case (which gave $U = \frac{3}{2}Nk_\mathrm{B}T$). The heat capacity C_V is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \tag{25.13}$$

and hence is given by[4] $C_V = 3Nk_\mathrm{B}$. The Helmholtz function is

$$F = -k_\mathrm{B}T\ln Z_N = -k_\mathrm{B}TN\ln V - 3Nk_\mathrm{B}T\ln T - k_\mathrm{B}T \times \text{constants}, \tag{25.14}$$

so that

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_\mathrm{B}T}{V} = nk_\mathrm{B}T, \tag{25.15}$$

which is the ideal gas equation,[5] as for the non-relativistic case. This also gives the enthalpy H via

$$H = U + pV = 4Nk_\mathrm{B}T. \tag{25.16}$$

As we found for the non-relativistic case, getting the entropy involves bothering with what the constants are in eqn 25.11. Hence, let us write this equation as

$$\begin{aligned} \ln Z_N &= N\ln V - 3N\ln\Lambda - N\ln N + N \\ &= N\ln\left(\frac{1}{n\Lambda^3}\right) + N, \end{aligned} \tag{25.17}$$

where $n = N/V$, so we immediately have (using the usual statistical mechanics manipulations listed in Table 20.1):

$$\begin{aligned} F &= -k_\mathrm{B}T\ln Z_N \\ &= Nk_\mathrm{B}T[\ln(n\Lambda^3) - 1], \end{aligned} \tag{25.18}$$

$$\begin{aligned} S &= \frac{U-F}{T} \\ &= Nk_\mathrm{B}\ln[4 - \ln(n\Lambda^3)], \end{aligned} \tag{25.19}$$

$$\begin{aligned} G &= H - TS = 4Nk_\mathrm{B}T - Nk_\mathrm{B}T[4 - \ln(n\Lambda^3)] \\ &= Nk_\mathrm{B}T\ln(n\Lambda^3). \end{aligned} \tag{25.20}$$

The results from this problem are summarized in Table 25.1.

One consequence of these results is that the pressure p is related to the energy density $u = U/V$ using

$$p = \frac{u}{3}, \tag{25.21}$$

which is very different from the non-relativistic case $p = 2u/3$ (see eqn 6.25). This has some rather dramatic consequences for the structure of stars (see Section 35.1.3).

[4] Notice that this does not agree with the equipartition theorem, which would predict $C_V = \frac{3}{2}Nk_\mathrm{B}$, half of the value that we have found. Why does the equipartition theorem fail? Because the dispersion relation is not a quadratic one (i.e. $E \propto p^2$), as is needed for the equipartition theorem to hold, but instead is a linear one ($E \propto p$).

[5] Note that we have $p = nk_\mathrm{B}T$ for both the non-relativistic and ultrarelativistic cases. This is because $Z_1 \propto V$ in both cases; hence $Z_N \propto V^N$ and $F = -k_\mathrm{B}TN\ln V+$(other terms not involving V), so that $p = -(\partial F/\partial V)_T = nk_\mathrm{B}T$.

Property	Non-relativistic	ultrarelativistic
Z_1	$\dfrac{V}{\lambda_{\mathrm{th}}^3}$ $\lambda_{\mathrm{th}} = \dfrac{h}{\sqrt{2\pi m k_{\mathrm{B}} T}}$	$\dfrac{V}{\Lambda^3}$ $\Lambda = \dfrac{\hbar c \pi^{2/3}}{k_{\mathrm{B}} T}$
U	$\frac{3}{2} N k_{\mathrm{B}} T$	$3 N k_{\mathrm{B}} T$
H	$\frac{5}{2} N k_{\mathrm{B}} T$	$4 N k_{\mathrm{B}} T$
p	$\dfrac{N k_{\mathrm{B}} T}{V}$ $= \dfrac{2u}{3}$	$\dfrac{N k_{\mathrm{B}} T}{V}$ $= \dfrac{u}{3}$
F	$N k_{\mathrm{B}} T [\ln(n \lambda_{\mathrm{th}}^3) - 1]$	$N k_{\mathrm{B}} T [\ln(n \Lambda^3) - 1]$
S	$N k_{\mathrm{B}} [\frac{5}{2} - \ln(n \lambda_{\mathrm{th}}^3)]$	$N k_{\mathrm{B}} [4 - \ln(n \Lambda^3)]$
G	$N k_{\mathrm{B}} T \ln(n \lambda_{\mathrm{th}}^3)$	$N k_{\mathrm{B}} T \ln(n \Lambda^3)$
Adiabatic expansion	$V T^{3/2} = \text{constant}$ $p V^{5/3} = \text{constant}$	$V T^3 = \text{constant}$ $p V^{4/3} = \text{constant}$

Table 25.1 The properties of non-relativistic and ultrarelativistic monatomic gases of indistinguishable particles of mass m.

25.3 Adiabatic expansion of an ultrarelativistic gas

We will now consider the adiabatic expansion of an ultrarelativistic monatomic gas. This means that we will keep the gas thermally isolated from its surroundings and no heat will enter or leave. The entropy stays constant in such a process, and hence (from Table 25.1) so does $n\Lambda^3$ which implies that

$$V T^3 = \text{constant}, \tag{25.22}$$

or equivalently (using $pV \propto T$)

$$p V^{4/3} = \text{constant}. \tag{25.23}$$

This implies that the adiabatic index $\gamma = 4/3$. This contrasts with the non-relativstic cases (for which $VT^{3/2}$ and $pV^{5/3}$ are constants, and $\gamma = 5/3$).

Example 25.2

An example of the adiabatic expansion of an ultrarelativistic gas relates to the expansion of the Universe. If the Universe expands adiabatically (how can heat enter or leave it when it presumably doesn't have any 'surroundings' by definition?) then we expect that an ultrarelativistic gas inside the Universe, such as the cosmic microwave background photons,[6] behaves according to

$$VT^3 = \text{constant}, \tag{25.24}$$

where T is the temperature of the Universe and V is its volume. Hence

$$T \propto V^{-1/3} \propto a^{-1}, \tag{25.25}$$

where a is the scale factor[7] of the Universe ($V \propto a^3$). Thus the temperature of the cosmic microwave background is inversely proportional to the scale factor of the Universe.

A non-relativistic gas in the Universe would behave according to

$$VT^{3/2} = \text{constant}, \tag{25.26}$$

in which case

$$T \propto V^{-2/3} \propto a^{-2}, \tag{25.27}$$

so the non-relativistic gas would cool faster than the cosmic microwave background as the Universe expands.

We can also work out the density ρ of both types of gas as a function of the scale factor a. For the adiabatic expansion of a gas of non-relativistic particles, the density $\rho \propto V^{-1}$ (because the mass stays constant) and hence

$$\rho \propto a^{-3}. \tag{25.28}$$

For relativistic particles,

$$\rho = \frac{u}{c^2}, \tag{25.29}$$

where $u = U/V$ is the energy density. Now $u = 3p$ (by eqn 25.21) and since $p \propto V^{-4/3}$ for relativistic particles, we have that

$$\rho \propto a^{-4}. \tag{25.30}$$

Thus the density drops off faster for a gas of relativistic particles than it does for non-relativistic particles, as the Universe expands.[8]

The Universe contains both matter (mostly non-relativistic) and photons (clearly ultrarelativistic). This simple analysis shows that as the Universe expanded, the matter cooled faster than the photons, but the density of the matter decreases less quickly than that due to the photons. The density of the early Universe is said to be **radiation dominated** but as time has passed the Universe has become **matter dominated** as far as its density (and hence expansion dynamics) is concerned.

[6] See Section 23.7.

[7] See Section 23.7.

[8] This is because, for both cases, you have the effect of volume dilution due to the Universe expanding which goes as a^3; but only for the relativistic case do you have an energy loss (and hence a density loss) due to the Universe expanding, giving an extra factor of a.

Chapter summary

- Using the ultrarelativistic dispersion relation $E = pc$, rather than the non-relativistic dispersion relation $E = p^2/2m$, leads to changes in various thermodynamic functions, as listed in Table 25.1.

Exercises

(25.1) Find the phase velocity and the group velocity for a relativistic particle whose energy E is $E^2 = p^2c^2 + m_0^2c^4$ and examine the limit $p \ll mc$ and $p \gg mc$.

(25.2) In D dimensions, show that the density of states of particles with spin-degeneracy g in a volume V is

$$g(k)\,\mathrm{d}k = \frac{gVD\pi^{D/2}k^{D-1}\,\mathrm{d}k}{\Gamma(\frac{D}{2}+1)(2\pi)^D}. \qquad (25.31)$$

You may need to use the fact that the volume of a sphere of radius r in D dimensions is (see Appendix C.8)

$$\frac{2\pi^{D/2}r^D}{\Gamma(\frac{D}{2}+1)}. \qquad (25.32)$$

(25.3) Consider a general dispersion relation of the form

$$E = \alpha p^s, \qquad (25.33)$$

where p is the momentum and α and p are constants. Using the result of the previous question, show that the density of states as a function of energy is

$$g(E)\,\mathrm{d}E = \frac{gVD\pi^{D/2}}{h^D\alpha^{D/s}s\Gamma(\frac{D}{2}+1)}E^{\frac{D}{s}-1}\,\mathrm{d}E. \qquad (25.34)$$

Hence show that the single-particle partition function takes the form

$$Z_1 = \frac{V}{\lambda^D}, \qquad (25.35)$$

where λ is given by

$$\lambda = \frac{h}{\pi^{1/2}}\left(\frac{\alpha}{k_{\mathrm{B}}T}\right)^{1/s}\left[\frac{\Gamma(\frac{D}{2}+1)}{\Gamma(\frac{D}{s}+1)}\right]^{1/D}. \qquad (25.36)$$

Show that this result for three dimensions ($D = 3$) agrees with (i) the non-relativistic case when $s = 2$ and (ii) the ultrarelativistic case when $s = 1$.