

Lecture notes 8

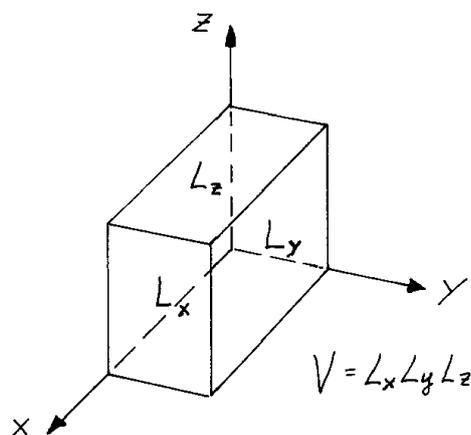
8. Three-dimensional box. Ideal Fermi and Bose gases

These notes start with the three-dimensional box (8.1), which is relevant e.g. when we consider an ideal gas of fermions (8.2) and the ideal Bose gas (8.3).

8.1 Three-dimensional box

[Hemmer 5.2, Griffiths p 193, B&J p 331]

8.1.a Energy levels



The figure shows a three-dimensional box with volume $V = L_x L_y L_z$, where the potential is zero inside the box and infinite outside. To find the energy eigenfunctions and the energy levels, we use the well-known results for the one-dimensional box:

$$\psi_{n_x}(x) = \sqrt{2/L_x} \sin k_{n_x} x; \quad k_{n_x} L_x = n_x \pi, \quad n_x = 1, 2, \dots$$

$$\widehat{H}_x \psi_{n_x}(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_{n_x}(x) = E_{n_x} \psi_{n_x}(x), \quad E_{n_x} = \frac{\hbar^2 k_{n_x}^2}{2m} = \frac{\pi^2 \hbar^2}{2m L_x^2} n_x^2.$$

In the three-dimensional case, the Hamiltonian is $\widehat{H} = \widehat{H}_x + \widehat{H}_y + \widehat{H}_z$, where all four operators commute. As energy eigenfunctions we may then use the product states

$$\psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin \frac{n_x \pi x}{L_x} \cdot \sin \frac{n_y \pi y}{L_y} \cdot \sin \frac{n_z \pi z}{L_z}, \quad (\text{T8.1})$$

which are simultaneous eigenfunctions of \widehat{H} , \widehat{H}_x , \widehat{H}_y and \widehat{H}_z (and which are equal to zero on the walls of the box). The energy eigenvalues are

$$E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right). \quad (\text{T8.2})$$

The eigenfunctions $\psi_{n_x n_y n_z}$ are normalized, and are also orthogonal, because we have only one such function for each combination of quantum numbers n_x , n_y , n_z . (Remember that two eigenfunctions of a hermitian operator with different eigenvalues are in general orthogonal.) Note that this means that the operators \widehat{H} , \widehat{H}_x , \widehat{H}_y and \widehat{H}_z are a so-called **complete set of commuting operators**.

8.1.b Symmetry leads to degeneracy

If two or three of the lengths L_x , L_y and L_z are chosen to be equal, some of the excited energy levels $E_{n_x n_y n_z}$ will “coincide”, that is, some of the energy levels become degenerate. As an example, with $L_x = L_y \neq L_z$, the states ψ_{211} and ψ_{121} get the same energy. With $L_x = L_y = L_z$, we get even more degeneracy. (Try to find the degeneracy for the lowest levels, and see B&J page 333.)

This shows that the degeneracy increases with increasing degree of symmetry. The same effect is observed for the three-dimensional harmonic oscillator.

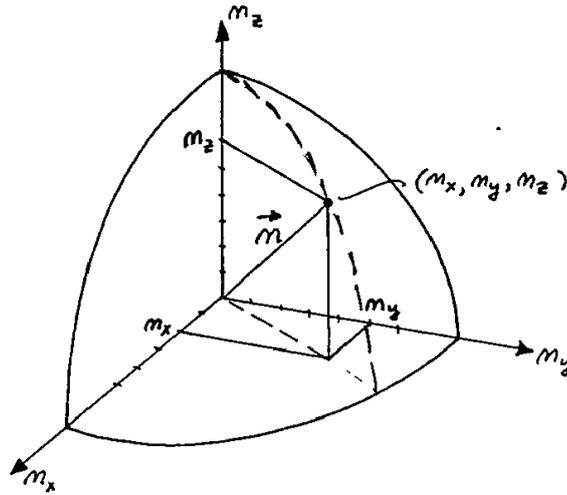
A small exercise: For a two-dimensional quadratic box you will find that the energies are proportional to $n_x^2 + n_y^2$. Use this to find the (degree of) degeneracy for the three lowest-lying energy levels. [Answer: 2,1,2.] Are you able to find a level with degeneracy 3? (Hint: Check the level with $n_x^2 + n_y^2 = 50$.)

8.1.c Density of states

An important application of the three-dimensional box is the quantum-mechanical description of **ideal gases**. We then consider a macroscopic volume $V = L_x L_y L_z$ containing a large number of identical particles (or large numbers of several particle species). The gas is considered to be ideal, in the sense that we are neglecting possible interactions between the particles.

For a macroscopic volume, the energy levels will be very closely spaced, and in the statistical treatment of such many-particle systems the number of quantum states (wave functions) per unit energy plays an important role. This is what is called the **density of states**.

We have one spatial state $\psi_{n_x n_y n_z}(x, y, z)$ for each combination n_x , n_y , n_z of positive integers. Each such combination corresponds to a “unit cell” (with volume 1) in “**n**-space”.



Simplifying to a cubical volume $V = L^3$, so that $E = \frac{\pi^2 \hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$, we note that the number $N_{\text{sp}}(E)$ of spatial wave functions with energy less than E is to a very good approximation given by the number of unit cells in the \mathbf{n} -space volume in the figure, which is $1/8$ of a sphere with radius

$$|\mathbf{n}| = \sqrt{n_x^2 + n_y^2 + n_z^2} = \sqrt{\frac{2mEL^2}{\pi^2 \hbar^2}}.$$

Thus the number of spatial states is

$$\begin{aligned} N_{\text{sp}}(E) &= \frac{1}{8} \cdot \frac{4\pi}{3} (n_x^2 + n_y^2 + n_z^2)^{3/2} = \frac{4\pi}{3} \left(\frac{2mEL^2}{4\pi^2 \hbar^2} \right)^{3/2} \\ &= \frac{4\pi}{3} \left(\frac{2m}{\hbar^2} \right)^{3/2} V E^{3/2}. \end{aligned} \quad (\text{T8.3})$$

We define the density of states, $g_{\text{sp}}(E)$, as the number of states per unit energy,

$$g_{\text{sp}}(E) = \frac{N(E + dE) - N(E)}{dE} = \frac{dN}{dE} = 2\pi \left(\frac{2m}{\hbar^2} \right)^{3/2} V E^{1/2}. \quad (\text{T8.4})$$

It can be shown (see e.g. Hemmer p 85) that this formula holds also for $L_x \neq L_y \neq L_z$. In fact, it can be shown that it holds for rather arbitrary forms of the volume V .

The fact that $g_{\text{sp}}(E)$ increases with the energy ($\propto \sqrt{E}$) is characteristic for three dimensions. If we go back to the *one-dimensional* box, the formula $E = (\pi^2 \hbar^2 / 2mL^2)n^2 = (\hbar^2 / 8mL^2)n^2$ tells us that the distance between the levels increases with the energy. Then the density of states (the number of states per unit energy) must of course *decrease*. Explicitly, we have that the number of eigenfunctions with energy less than E is

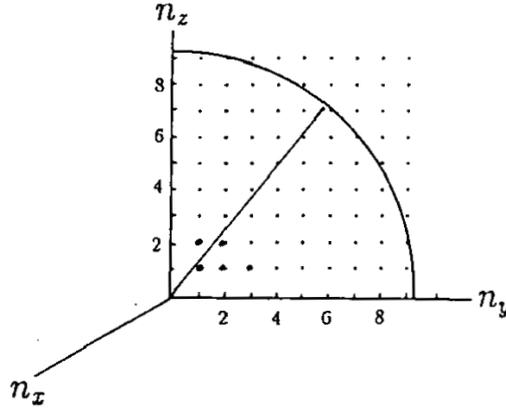
$$N_{\text{sp}}^{(1)}(E) = n = \sqrt{\frac{8mL^2}{\hbar^2} E}.$$

Then the decrease of the density of states with increasing energy goes as

$$g_{\text{sp}}^{(1)}(E) = \frac{dN}{dE} = \sqrt{\frac{2m}{\hbar^2}} \cdot L \cdot E^{-1/2}. \quad (\text{T8.5})$$

For particles that are confined to move in *two* dimensions (on an area $A = L^2$), it follows in the same manner from the formula $E = (\hbar^2/8mL^2)(n_y^2 + n_z^2)$ that the number of states with energy less than E is

$$N_{\text{sp}}^{(2)}(E) = \frac{1}{4} \cdot \pi(n_y^2 + n_z^2) = \frac{2\pi mL^2}{h^2} E. \tag{T8.6}$$



Here the density of states is *constant*,

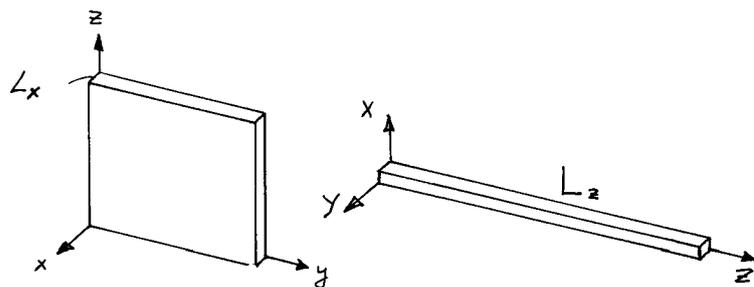
$$g_{\text{sp}}^{(2)}(E) = \frac{dN}{dE} = \frac{2\pi m}{h^2} \cdot L^2. \tag{T8.7}$$

You should note that one- or two-dimensional systems are not purely theoretical constructions. By choosing e.g. a three-dimensional box (or potential well) with very small L_x , while L_y and L_z are large or even macroscopic, we see that the energy $\pi^2\hbar^2/(2mL_x^2)$ in the formula

$$E_{n_x n_y n_z} = \frac{\pi^2\hbar^2}{2mL_x^2} n_x^2 + \frac{\pi^2\hbar^2}{2mL_y^2} n_y^2 + \frac{\pi^2\hbar^2}{2mL_z^2} n_z^2$$

becomes very much larger than $\pi^2\hbar^2/(2mL_y^2)$ and $\pi^2\hbar^2/(2mL_z^2)$. This may imply that the particle (or particles) moving in this kind of well is in practice never excited to states with $n_x > 1$. The x -dependent part of the wave function then is fixed to $\psi_1(x) = \sqrt{2/L_x} \sin \pi x/L_x$. In such a case, “nothing happens” with the motion in the x -direction. At the same time, only small amounts of energy are needed to excite the y - and z -degrees of freedom. Thus the “physical processes will be going on in these directions”, and the system is effectively two-dimensional.

In a similar manner we can make a system effectively one-dimensional by choosing both L_x and L_y to be very small, while the “longitudinal” dimension L_z is large (as shown in the figure on the right):



The energies corresponding to the lowest-lying (longitudinal) states $\psi_{n_z}(z)$ then become very small compared with the energies needed to excite the transverse degrees of freedom. This means that “interesting physics” may be going on “longitudinally” (involving the z -direction), while the transverse degrees of freedom are “frozen”, giving an effective one-dimensional system.

8.1.d Periodic boundary conditions

(Hemmer p 86, Griffiths p 199, B&J p 331)

For the effectively “one-dimensional” box just mentioned, we have seen that the ordinary boundary conditions (the “box conditions” $\psi(0) = \psi(L_z) = 0$) give energy eigenfunctions in the form of standing waves, $\psi_{n_z}(z) = \sqrt{2/L_z} \sin(\pi n_z z/L_z)$. As explained in the references cited above, it is often customary to replace these standing waves with *running* waves in the form of momentum eigenfunctions,

$$\psi(z) = \frac{1}{\sqrt{L_z}} e^{ikz},$$

while replacing the “box conditions” by so-called **periodic boundary conditions**:

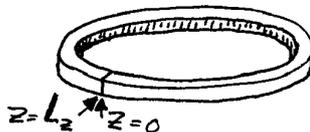
$$\boxed{\psi(0) = \psi(L_z),} \quad \implies \quad e^{ikL_z} = 1 \quad \implies \quad kL_z = 2\pi n, \quad \implies \quad (\text{T8.8})$$

$$k_n = \frac{2\pi n}{L_z}, \quad p_n = \hbar k_n = \frac{nh}{L_z}, \quad E_n = \frac{\hbar^2 k_n^2}{2m}, \quad n = 0, \pm 1, \pm 2, \dots$$

These energy eigenfunctions are normalized, and it is easy to see that they are also orthogonal (because they are momentum eigenfunctions, each with their own momentum eigenvalue p_n):

$$\int_0^{L_z} \psi_{n_1}^*(z) \psi_{n_2}(z) dz = \delta_{n_1 n_2}. \quad (\text{T8.9})$$

In many problems, the use of periodic boundary conditions is as relevant as the original conditions. For the “one-dimensional” box above, we can motivate this statement by noting that the physics of this box will not be seriously altered (except for the disappearance of certain boundary effects) if we bend it around so that it is changed into a “ring”.

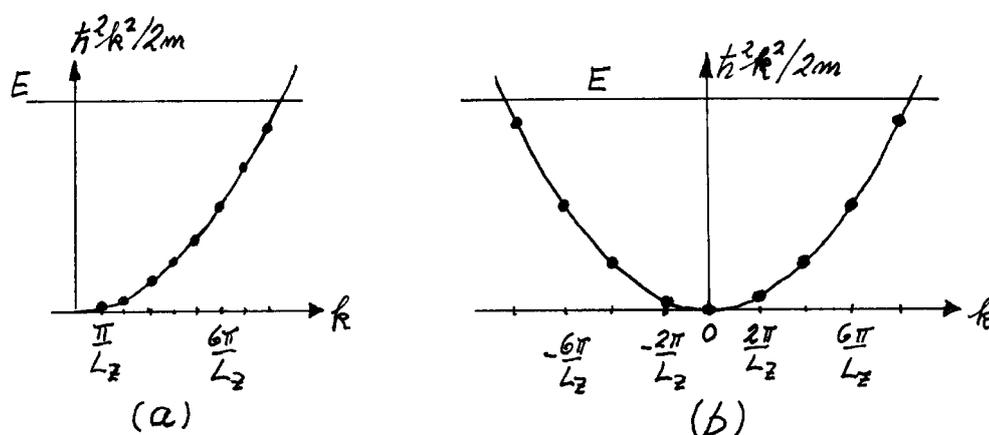


For this ring, the relevant condition is $\psi(0) = \psi(L_z)$. Even if we do not “bend the box into a ring”, the boundary effects mentioned are not very important for macroscopic L_z . Thus, we may just as well use periodic boundary conditions to find e.g. the density of states.

For a three-dimensional box (modeling e.g. the three-dimensional well occupied by the conduction electrons in a piece of metal) it is impossible to imagine how to bend it around so that opposite sides could be “welded” together. However, when we are not particularly interested in boundary (or surface) effects, but rather in bulk properties, we may also here just as well use periodic boundary conditions.

In certain problems, periodic boundary conditions are even *more* relevant than box conditions. This is the case e.g. in three-dimensional scattering calculations. Then incoming and outgoing particles are most suitably represented by momentum wave functions. Such calculations are often simplified by placing the system inside a fictitious volume, in the form of a cubical box. One then uses periodic boundary conditions, corresponding to normalized wave functions and discrete momenta.

It should be noted that periodic boundary conditions give the same density of states as the original box conditions. In one dimension we saw above that periodic boundary conditions give wave numbers $k_n = 2\pi n/L_z$ half as densely spaced (see figure (b) below) as the wave numbers $k_{n_z} = \pi n_z/L_z$ obtained with ordinary box conditions (see figure (a) below).



However, as shown in the figure, this is compensated by the former taking both positive and negative values. Thus the number $N_{\text{sp}}^{(1)}(E)$ of states with energy less than E is the same for both types of boundary conditions, and the same then holds for the density of states.

Let us see how the periodic boundary conditions work in three dimensions. The orthonormal momentum eigenfunctions then are

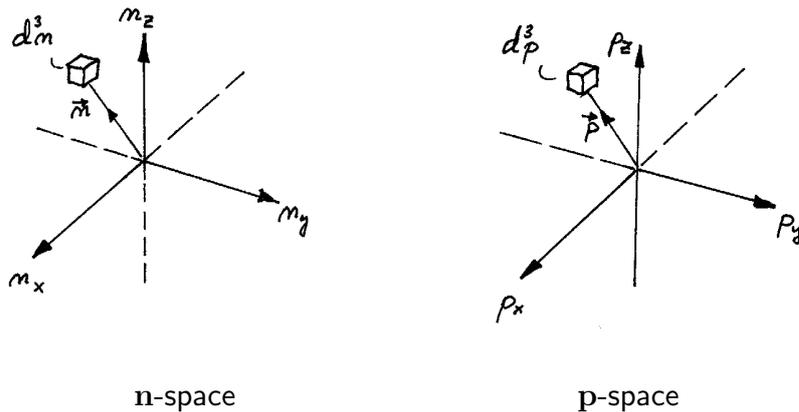
$$\psi_{n_x n_y n_z} = \frac{1}{\sqrt{L_x L_y L_z}} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (\text{T8.10})$$

where

$$k_x = \frac{2\pi n_x}{L_x}, \quad p_x = \hbar k_x = \frac{h}{L_x} n_x, \quad n_x = 0, \pm 1, \pm 2, \dots,$$

and similarly for k_y and k_z . A straightforward way to obtain the density of states is as follows: From the relations $k_x = 2\pi n_x/L_x$ etc we have that $dk_x = 2\pi \cdot dn_x/L_x$ etc, so that

$$d^3k = dk_x dk_y dk_z = \frac{(2\pi)^3}{L_x L_y L_z} dn_x dn_y dn_z = \frac{(2\pi)^3}{V} d^3n.$$



n-space now includes all eight octants (contrary to the octant on page 2). In this space we have one state per unit volume. The number of states in the volume element d^3n in this space thus equals d^3n . From the above relation between d^3k and d^3n we may then state that the number of momentum states in the volume element d^3k of **k-space** (i.e. the number in d^3p in **p-space**) is

$$dN_{\text{sp}} = d^3n = \frac{V d^3k}{(2\pi)^3} = \frac{V d^3p}{h^3}. \quad (\text{T8.11})$$

This formula (and its generalization in the footnote)¹ is a common starting point in the calculation of densities of states, both non-relativistically and in relativistic calculations. The formulae (T8.10) and (T8.11) are valid relativistically.

Let us try to calculate relativistically, using the formulae

$$E = \frac{mc^2}{\sqrt{1 - v^2/c^2}} \equiv \gamma mc^2, \quad \mathbf{p} = \gamma m \mathbf{v}, \quad (\text{T8.12})$$

$$\frac{c^2 \mathbf{p}}{E} = \frac{c^2 \gamma m \mathbf{v}}{\gamma mc^2} = \mathbf{v}, \quad E^2 = c^2 p^2 + m^2 c^4.$$

From the last two formulae we have that

$$2E dE = c^2 2p dp, \quad \text{that is,} \quad \frac{dp}{dE} = \frac{E}{c^2 p} = \frac{1}{v}. \quad (\text{T8.13})$$

Armed with these formulae we first note that all states with energy less than $E = \sqrt{c^2 p^2 + m^2 c^4}$ correspond to points in **p-space** inside a sphere with radius p . According to (T8.11) the num-

¹The formula (T8.11) above may be generalized to the following rule: The number of spatial states in the element $d^3r d^3p$ of the 6-dimensional **phase space** is

$$dN = \frac{d^3r d^3p}{h^3}.$$

This formula is easy to remember because

Each spatial state occupies a “volume” h^3 in **phase space**.

ber then is

$$N_{\text{sp}}^{(\text{Rel})}(E) = \frac{V}{h^3} \frac{4\pi p^3}{3}. \quad \left(\begin{array}{l} \text{Number of states} \\ \text{with momentum } < p, \\ \text{relativistically.} \end{array} \right) \quad (\text{T8.14})$$

This is the relativistic generalization of (T8.3). States with energies in the interval $(E, E + dE)$, that is, with momenta in the interval $(p, p + dp)$, correspond to points inside a *spherical shell* in \mathbf{p} -space:

$$dN_{\text{sp}}^{(\text{Rel})}(E) = \frac{V}{h^3} \cdot 4\pi p^2 dp.$$

The relativistic formula for the density of states then becomes (using (T8.13))

$$g_{\text{sp}}^{\text{Rel}}(E) = \frac{dN}{dE} = \frac{4\pi V}{h^3} \frac{p^2}{v}. \quad \left(\begin{array}{l} \text{density of} \\ \text{spatial states,} \\ \text{relativistically.} \end{array} \right) \quad (\text{T8.15})$$

In the non-relativistic limit (with $p^2/v = mp = m\sqrt{2mE}$) this formula yields equation (T8.4):

$$g_{\text{sp}}(E) = 2\pi \left(\frac{2m}{h^2} \right)^{3/2} V E^{1/2}. \quad \left(\begin{array}{l} \text{Density of} \\ \text{spatial states,} \\ \text{non-relativistically.} \end{array} \right) \quad (\text{T8.16})$$

The relativistic formulae above hold not only for particles, that is for de Broglie waves, but also for electromagnetic waves, for which the periodic boundary conditions give exactly the same allowed values as above for the wave number \mathbf{k} (and the momentum $\mathbf{p} = \hbar\mathbf{k}$ of the photons). Photons have $v = c$ and $p = E/c = h\nu/c$. When we include an extra factor 2 to account for the two possible polarizations for each photon, we find that the number of **photon modes** with frequency in the interval $(\nu, \nu + d\nu)$ is

$$dN_{\text{ph}} = 2 \frac{V \cdot 4\pi p^2 dp}{h^3} = \frac{8\pi V}{c^3} \nu^2 d\nu. \quad (\text{T8.17})$$

This formula plays an important role in the derivation of Planck's law, as we shall see later.

8.2 Ideal gas of spin- $\frac{1}{2}$ fermions

(Hemmer p 195, Griffiths p 193, B&J p 478)

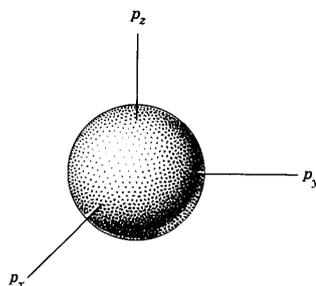
8.2.a Fermi gas at low temperatures, generalities

In the ideal-gas approximation we assume that there are no forces acting between the N identical spin- $\frac{1}{2}$ fermions inside the box volume $V = L_x L_y L_z$. (Thus the only forces acting are those from the confining walls.)

Real gases are *not ideal*, and *real* fermion systems are not ideal Fermi gases. However, some of the properties of real systems are fairly well described by the ideal-gas approximation. Later we shall use this ideal model to describe essential properties of e.g. the conduction electrons in a metal.

If these particles were *bosons*, the ground state of the system would correspond to all of the particles being in the box state $\psi_{111} \propto \sin(\pi x/L_x) \sin(\pi y/L_y) \sin(\pi z/L_z)$. However, since they are spin- $\frac{1}{2}$ fermions, Pauli's exclusion principle allows only one particle in each quantum-mechanical one-particle state, that is, two particles with opposite spins in each spatial state. With a large number N of particles in the volume V , this means that most of them are forced to occupy one-particle states with large quantum numbers.

This holds even for the **ground state of the many-particle system**, which is the state with the lowest possible total energy. It is easy to find this ground state. Let us use the one-particle states corresponding to periodic boundary conditions, and imagine that we add the particles one after one. The first few particles will then choose the spatial one-particle states $\psi_{n_x n_y n_z}$ with the lowest quantum numbers, represented by points $\mathbf{p} = \{p_x, p_y, p_z\} = h\{n_x/L_x, n_y/L_y, n_z/L_z\}$ close to the origin in \mathbf{p} -space. However, as more and more particles enter, the value of $|\mathbf{p}|$ for the lowest-lying unoccupied state becomes larger and larger. This means of course that when all the N particles have been added, they will occupy all states inside a sphere in \mathbf{p} -space, with all states inside occupied and all states outside unoccupied. This is the state with the lowest possible total energy, that is, the ground state of this many-particle system. (A state with one or more unoccupied states inside this sphere and the same number of occupied states outside has a higher total energy, and is an excited state of the many-particle system.)



Thus the N fermions in the volume V have momenta $|\mathbf{p}|$ ranging from zero up to a maximal momentum p_F given by the radius of this sphere. The radius p_F of this sphere is called the **Fermi momentum** and the corresponding kinetic energy ($E_F = p_F^2/2m$ in the non-relativistic case) is the so-called **Fermi energy**. To find p_F , we only have to remember that

the number of states in the element d^3p of \mathbf{p} -space is now

$$dN = 2 dN_{\text{sp}} = 2 \frac{V d^3p}{h^3}, \quad (\text{T8.18})$$

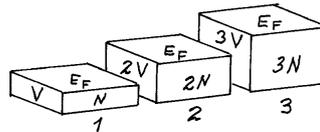
where the factor 2 counts the two spin directions. Equating the particle number N with the total number of states inside the **Fermi sphere**, we then have

$$N = 2 \frac{V}{h^3} \frac{4\pi p_F^3}{3}. \quad (\text{T8.19})$$

Thus we see that even in the ground state of this many-particle system the particles have momenta and kinetic energies ranging from zero up to maximal values given by the Fermi momentum and the Fermi energy, which are

$$p_F = \hbar \left(3\pi^2 \frac{N}{V} \right)^{1/3} \quad \text{og} \quad E_F = \frac{p_F^2}{2m} = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3}. \quad (\text{T8.20})$$

This property of the Fermi gas has far-reaching consequences. First of all we note that it is the **number density** N/V of the fermions that matters. Thus, the Fermi energy in box 1 and box 2 are the same, and if we “merge” box 1 and box 2 as in box 3, the Fermi energy still is the same.



This illustrates the fact that the bulk properties of the Fermi gas are independent of the form and size of the macroscopic volume (and of the boundary conditions used). Note also that for a given N/V , the (non-relativistic) Fermi energy is inversely proportional to the mass. Thus, this effect of the exclusion principle is most pronounced for the lightest particles.

Next, imagine that we keep V constant and increase N , say by a factor $8 = 2^3$. Then, due to the exclusion principle, the radius p_F of the Fermi sphere increases with a factor 2, and the Fermi energy $E_F = p_F^2/2m$ increases with a factor 4, and so does the average kinetic energy $\langle E \rangle$.

The same result is obtained by reducing the volume V , since E_F is proportional to $V^{-2/3}$. If we set $V = L^3$, each of the one-particle energies and hence also E_F and E_{tot} increase as $1/L^2$ for decreasing L . This behaviour of the Fermi gas is very important, e.g. in white dwarfs.

Total kinetic energy E_{tot} and the average $\langle E \rangle$ (non-relativistic)

To find the total kinetic energy E_{tot} in the ground state of this N -fermion-system we only need to sum up the energies of the one-particle states inside the Fermi sphere:

$$\begin{aligned} E_{\text{tot}} &= \int E dN = \int_0^{p_F} \frac{p^2}{2m} \cdot 2 \frac{V d^3p}{h^3} && (d^3p = 4\pi p^2 dp) \\ &= \frac{2V}{h^3} \frac{4\pi}{2m} \int_0^{p_F} p^4 dp = \underbrace{\frac{2V}{h^3} \frac{4\pi p_F^3}{3}}_N \frac{3}{5} \underbrace{\frac{p_F^2}{2m}}_{E_F}. \end{aligned}$$

Thus the total kinetic energy is

$$E_{\text{tot}} = \frac{3}{5} N E_F, \quad (\text{T8.21})$$

and the average kinetic energy of the N fermions is

$$\langle E \rangle = \frac{3}{5} E_F. \quad (\text{T8.22})$$

[You should perhaps check that the integral $E_{\text{tot}} = \int_0^{E_F} E g(E) dE$, with $g(E) = 2g_{\text{sp}}(E)$, gives the same result.]

A small exercise: A box with volume $V = L^3$ contains 14 electrons. What is the highest one-particle energy (the Fermi energy) when the system is in the ground state, which is the state with the lowest total energy for the 14 electrons? What is the average energy of these electrons in the ground state? [Answer: The highest one-particle energy is that of the state with $n_x^2 + n_y^2 + n_z^2 = 9$. In average, we have $n_x^2 + n_y^2 + n_z^2 = 6.857$.]

The Pauli (or quantum) pressure

It is interesting to note that if we keep N constant and let V increase, the total internal energy decreases, because E_{tot} goes as $E_{\text{tot}} = \text{constant} \cdot V^{-2/3}$:

$$E_{\text{tot}} = \frac{3}{5} N \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3} \equiv \text{konstant} \cdot V^{-2/3}.$$

With

$$\frac{\partial E_{\text{tot}}}{\partial V} = -\frac{2}{3} \cdot \text{konstant} \cdot V^{-5/3} = -\frac{2}{3} \frac{E_{\text{tot}}}{V},$$

we then find that an infinitesimal increase ΔV of the volume corresponds to a change of the total ground-state energy by the amount

$$\Delta E_{\text{tot}} = \frac{\partial E_{\text{tot}}}{\partial V} \Delta V = -\frac{2}{3} \frac{E_{\text{tot}}}{V} \Delta V.$$

To find out what happens with the “lost” energy amount $|\Delta E_{\text{tot}}| = -\Delta E_{\text{tot}}$, we must realize that the Fermi gas exerts a *pressure* P on the walls of the volume. This means that $|\Delta E_{\text{tot}}|$ is not lost, but is spent doing a work $P\Delta V = -\Delta E_{\text{tot}}$ “on the outside”. The conclusion is that the Fermi gas exerts a pressure

$$P = -\frac{\partial E_{\text{tot}}}{\partial V} = \frac{2}{3} \frac{E_{\text{tot}}}{V} \quad (\text{T8.23})$$

on the walls of the box. Inserting for E_{tot} we find that

$$P = \frac{2}{5} \frac{N}{V} E_F = \frac{\pi^{4/3} \hbar^2}{15m} \left(3 \frac{N}{V} \right)^{5/3}. \quad (\text{T8.24})$$

To see what this means, we note that the ground state, which is considered here, strictly speaking describes the system in the zero-temperature limit, $T \rightarrow 0$. In this limit, the pressure $P_{\text{cl}} = Nk_B T/V$ of a *classical* ideal gas goes to zero. ($k_B = 1.38066 \times 10^{-23}$ J/K = 0.682×10^{-4} eV/K is Boltzmann’s constant.) This is contrary to the **quantum**

pressure we have found here, which does not go away as $T \rightarrow 0$. This pressure has nothing to do with thermal motion, and is sometimes called the **Pauli pressure**. An even better name would be **exclusion pressure**, because it is the exclusion principle which makes the Fermi sphere so large and the pressure so high.

At moderate temperatures, this exclusion pressure is much larger than the pressure expected from the classical ideal-gas formula $P = NkT/V$. To see this, we must look into what happens with the state of the Fermi gas at “low” temperatures.

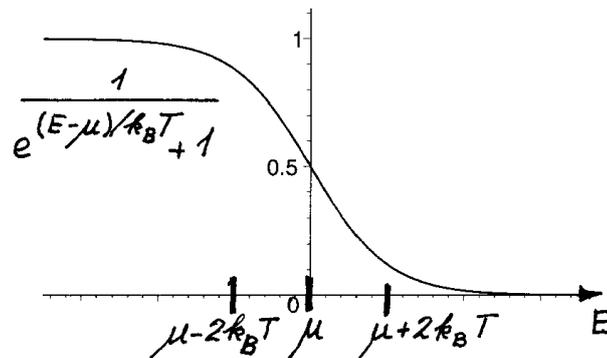
The Fermi gas at “low” temperatures. The Fermi–Dirac distribution

To describe the state of this many-particle system of identical fermions at a temperature $T > 0$ we have to invoke some results *outside* quantum mechanics, namely some central results from another important physical theory, **quantum statistical mechanics** (cf TFY4230 Statistical Physics):

At “low” temperatures, that is, when the “thermal” energy amount $k_B T$ is small compared to the Fermi energy E_F , the state of the gas does not differ much from the ground state: A few of the fermions have been excited, from states *just inside* the **Fermi surface** ($E_F - k_B T \lesssim E < E_F$) to states *just outside* ($E_F < E \lesssim E_F + k_B T$). Thus, inside and close to the surface the probability of finding a state occupied is slightly smaller than 1, while it is slightly larger than zero for states outside and close to the surface. This probability (for a given one-particle state) is called the **occupation number**; it gives the *average* number $\langle n \rangle$ of fermions occupying the one-particle state in question. (Even in thermodynamic equilibrium there are fluctuations. A state can be occupied one moment, and unoccupied in the next.) According to the exclusion principle this occupation number must lie between zero and 1. In statistical mechanics one learns that it is given by the so-called **Fermi–Dirac-distribution**:

$$\boxed{\langle n \rangle = \frac{1}{e^{(E-\mu)/k_B T} + 1}}, \quad \left(\begin{array}{l} \text{Fermi–Dirac} \\ \text{distribution} \end{array} \right) \quad (\text{T8.25})$$

According to this distribution law the occupation number in general decreases with increasing one-particle energy E . We note also that the change from large ($\gtrsim 1$) to small ($\lesssim 0$) occupation numbers takes place in an energy interval of the order of a few $k_B T$ (cf the discussion above). As shown in the figure, this energy interval is centered around the energy value μ , which is the E -value for which $\langle n \rangle$ equals 50%.



This energy value μ is called the **chemical potential** for the fermion system in question. What makes this law a bit difficult to grasp, is the fact that μ in principle depends on the temperature, and also on the other system parameters (V , m and N). Luckily, it can be stated that

For “low” temperatures, $k_B T \ll E_F$, we may in practice set

$$\mu(T) \approx \mu(0) = E_F. \tag{T8.26}$$

The arguments behind this statement are as follows:

(i) In the limit $T \rightarrow 0$, we see from the formula for $\langle n \rangle$ and from the figure above that the change from $n = 1$ to $n = 0$ happens very quickly: In this limit we have

$$\lim_{T \rightarrow 0} \frac{dN}{dE} = \begin{cases} g(E) & \text{for } E < \mu(0), \\ 0 & \text{for } E > \mu(0). \end{cases}$$

Thus, for $T = 0$ all states with $E < \mu(0)$ (and no states for $E > \mu(0)$) are occupied. But this was precisely how the Fermi energy was defined. Thus,

$$\mu(0) = E_F, \tag{T8.27}$$

and we see that The Fermi–Dirac distribution predicts that the system is in the ground state at $T = 0$, as it should.

(ii) That the chemical potential μ depends on the temperature can be understood from the following argument: With $g(E)dE$ states in the interval $(E, E + dE)$, the expected number of fermions in this interval is

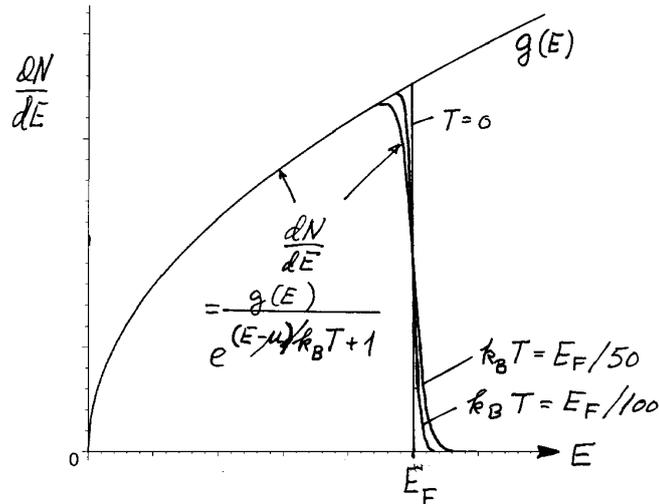
$$dN = \langle n \rangle g(E)dE = \frac{g(E)dE}{e^{(E-\mu)/k_B T} + 1}. \tag{T8.28}$$

Integrated over all energies this should give the total number N of fermions in the volume V :

$$N = \int_0^\infty \frac{g(E)dE}{e^{(E-\mu)/k_B T} + 1}. \tag{T8.29}$$

For given values of V and m the density of states $g(E)$ is a well-defined function of the energy. Then, for a given temperature T , the integral can only be equal to N for one particular value of μ , which is thus a function of T ; we have $\mu = \mu(T)$.

(iii) The fact that the difference between $\mu(T)$ and $\mu(0) = E_F$ is small for $k_B T \ll E_F$ can be understood from the figure below:

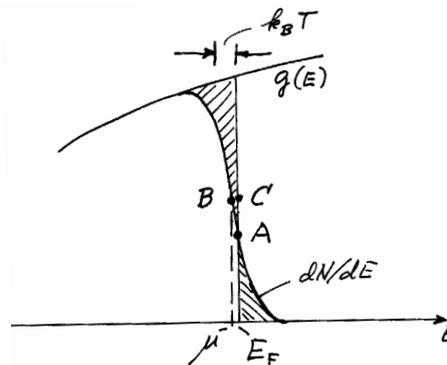


This graph shows the number of *states* per energy unit, $g(E) \propto \sqrt{E}$, and the expected number of *fermions* per energy unit,

$$\frac{dN}{dE} = g(E) \langle n \rangle = \frac{g(E)}{e^{(E-\mu)/k_B T} + 1},$$

for three cases: $k_B T/E_F = 0$, $1/100$ and $1/50$. Here, we note that the area under the curve for $T = 0$ (that is, under $g(E)$ up to $E = E_F$) equals the number N of fermions. Of course, the same holds also for the areas under the two curves for $T > 0$. (Cf the integral (T8.28).)

This means that the two hatched areas in the figure below, above and below the point A, respectively, must be equal. These areas represent the number of *unoccupied* states inside the Fermi surface and the number of *occupied* states outside, respectively.)



At the point B in the figure, the value of dN/dE is 50% of $g(E)$, so the abscissa of B is the chemical potential μ . Point C lies “midway” on the “ E_F -line”. In the figure, we have exaggerated the difference between μ and E_F , and also the distance between A and C. Since the two areas are equal, we understand that point A must in reality lie very close to point C, that is, point A must lie *almost* midway on the “ E_F -line”. (Actually, it must lie a *little bit* below the midpoint, because $g(E)$ decreases weakly as a function of the energy.) Thus,

$$\left. \frac{dN}{dE} \right|_{E_F} = \frac{g(E_F)}{e^{(E_F-\mu)/k_B T} + 1} \approx \frac{1}{2}g(E_F).$$

This means that $e^{(E_F - \mu/k_B T)} \approx 1$, that is, $E_F - \mu \ll k_B T$. It can be shown that the difference between $\mu(T)$ and $E_F = \mu(0)$ is of second order in $k_B T/E_F$:

$$\mu(T) \approx E_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 \right] \quad (k_B T \ll E_F). \quad (\text{T8.30})$$

Thus, as suggested, the chemical potential μ *decreases* slightly with increasing temperature, but only to second order in the “smallness parameter” $k_B T/E_F$. When this ratio is small, we can therefore use (T8.25), $\mu(T) \approx \mu(0) = E_F$, for most purposes.²

From the graphs above, one can also understand that for $k_B T \ll E_F$ the increase in the total energy E_{tot} is small compared to the value at $T = 0$, which is $\frac{3}{5} N E_F$. The *fraction* of excited fermions (cf the hatched areas) is of the order of the smallness parameter $k_B T/E_F$, and the same can be said about the energy increase for these particles ($\sim k_B T$) compared to the average energy $\langle E \rangle$. This means that also the increase of the total energy E_{tot} becomes a second-order effect. It can be shown that

$$E_{\text{tot}} = E_{\text{tot}}(0) + N \frac{\pi^2}{4} \frac{k_B^2 T^2}{E_F} \left(= \frac{3}{5} N E_F \left[1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 \right] \right). \quad (\text{T8.31})$$

This means (among other things) that the exclusion pressure $P = 2E_{\text{tot}}/3V$ of the “low”-temperature Fermi gas is almost the same as for $T = 0$; the “thermal” part of the motion is almost negligible compared to the effect of the exclusion principle. As stated above, this means that the exclusion pressure is much higher than we would expect from the classical ideal-gas law $P_{\text{cl}} = N k_B T/V$. Using $E_{\text{tot}} \approx E_{\text{tot}}(T = 0) = \frac{3}{5} N E_F$, we find the ratio

$$\frac{P}{P_{\text{cl}}} = \frac{2E_{\text{tot}}/3V}{N k_B T/V} \approx \frac{2}{5} \frac{E_F}{k_B T} \quad (k_B T \ll E_F). \quad (\text{T8.32})$$

The bottom line of this discussion is that the “cold” Fermi gas (with $T \ll T_F \equiv E_F/k_B$) behaves in several respects almost as in the ground state (for $T = 0$), with

$$P = \frac{\pi^{4/3} \hbar^2}{15m} \left(3 \frac{N}{V} \right)^{5/3} \quad (T \ll E_F/k_B \equiv T_F). \quad (\text{T8.33})$$

Thus this relation is to a good approximation the **equation of state** for the Fermi gas when T is much smaller than the **Fermi temperature**, $T_F \equiv E_F/k_B$.³

It turns out that the ideal Fermi-gas model can be applied with some success to several important physical systems. We have already mentioned the conduction electrons in metals, for which the model provides important insight. Another example is nuclear matter (in nuclei and neutron stars), where this simple model gives some insight, and electrons in white-dwarf stars. In all these cases, it turns out that the actual temperatures are low compared to $T_F \equiv E_F/k_B$.

²A small thought experiment reveals that the chemical potential $\mu(T)$ becomes considerably smaller than E_F and perhaps even becomes negative, if the temperature is sufficiently high: If we heat our Fermi gas to extremely high temperatures, $T \gg E_F/k_B$, then almost all the fermions will be excited to one-particle states with high energies. Since the number of available states is unlimited, we realize that the occupation numbers can then very well become less than 50% even for the “lowest” one-particle states (with $E \approx 0$). According to (T8.25), $\mu(T)$ must then be smaller than the lowest energies, that is, negative.

³The Fermi temperature $T_F \equiv E_F/k_B$ depends on the system. It is the temperature for which $k_B T$ becomes equal to the Fermi energy E_F . This means that T_F increases with increasing N/V .

8.2.b Free-electron-gas model for conduction electrons in metals

(Hemmer p 195, Griffiths p 193, B&J p 483)

In a crystalline solid most of the electrons are bound to the nuclei at the lattice points, forming a lattice of positive ions, but if it is a metallic conductor some electrons from the outer subshells of the atoms are relatively free to move through the solid. These are the **conduction electrons**. Because the charges of these electrons are cancelled by those of the ions, they move around approximately as neutral free fermions.

The actual potential seen by each conduction electron in a metal is a **periodic** or almost periodic potential in three dimensions, depending on whether the lattice of positive ions is that of a perfect or almost perfect crystal. In the *free-electron model*, this periodic potential is replaced by a smoothed-out constant potential, with the metal boundaries acting as high potential walls. A macroscopic potential well of this type is excellently represented by a three-dimensional box. This gives us a simplified model in which the conduction electrons behave as “neutral” fermions, moving without interacting with other particles inside the box. That is, we are treating the conduction electrons as an ideal Fermi gas.

Densities of state and Fermi energies

The Fermi energy (T8.20) of the conduction electrons can be written as

$$E_F = \frac{p_F^2}{2m_e} = \frac{\hbar^2}{2m_e} \left(3\pi^2 \frac{N}{V} \right)^{2/3} = \frac{\hbar^2}{2m_e a_0^2} (3\pi^2 a_0^3 \frac{N}{V})^{2/3},$$

where $\hbar^2/2m_e a_0^2 = 13.6 \text{ eV}$ is the Rydberg energy. From this formula it is evident that E_F must be of “atomic” size, because the volume V/N per conduction electron must be of the same size as the atomic volume, that is, equal to a_0^3 or thereabout.

For a more accurate calculation of N/V , we need to know the number Z_l of conduction electrons per atom. This number varies from 1 to 5 for the various elements. We also need the accurate number of atoms per unit volume, N_a/V , which depends on the mass density ρ_m and the atomic mass. The latter is

$$m = \frac{A}{N_A},$$

where A is the atomic weight (grams per mole) and $N_A = 0.6022 \times 10^{24}$ atoms per mole is **Avogadro’s number**. Since $mN_a = \rho_m V$, we have that

$$\frac{N_a}{V} = \frac{\rho_m}{m} = N_A \frac{\rho_m}{A}.$$

Thus the number density of conduction electrons is

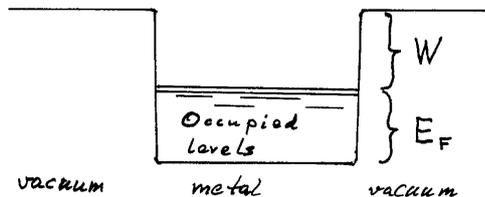
$$\frac{N}{V} = Z_l \frac{N_a}{V} = N_A \frac{Z_l \rho_m}{A}. \quad (\text{T8.34})$$

Using this formula one finds that N/V in metals varies from 0.91×10^{22} per cm^3 for cesium, to 24.7×10^{22} per cm^3 for beryllium. The table below gives N/V and the resulting Fermi energies E_F for a selection of metals. As you can see, the energies E_F are of “atomic” size, as expected.

Element	Z_c	N/V (10^{22}cm^{-3})	E_F (eV)	T_F (10^4K)	W (eV)
Li	1	4.70	4.74	5.51	2.38
K	1	1.40	2.12	2.46	2.22
Cu	1	8.47	7.00	8.16	4.4
Ag	1	5.86	5.49	6.38	4.3
Au	1	5.90	5.53	6.42	4.3
Be	2	24.7	14.3	16.6	3.92
Al	3	18.1	11.7	13.6	4.25

(From Ashcroft & Mermin, *Solid State Physics*.)

The table also includes the Fermi temperatures $T_F = E_F/k_B$, and the work functions W ; the latter are experimental numbers. The work function is the energy required to liberate an electron at the Fermi surface from the metal. According to this model, the depth of the potential well mentioned earlier is the sum of E_F and W , which comes out typically as a number of the order of 10 eV.



The most striking feature of these results is that, due to the large number densities N/V , the Fermi energies are *much larger* than the typical *thermal* energy $k_B T$ at room temperature (300 K), $k_B T \approx 0.026\text{ eV} \approx 1/40\text{ eV}$. Another way to express the same thing is to note that the Fermi temperatures $T_F \equiv E_F/k_B$ are very large, of the order of 10^4 K . This means that we have a “cold” Fermi gas of conduction electrons.

Exclusion pressure and bulk modulus

For copper the Fermi energy $E_F = 7.00\text{ eV}$ and the number density $N/V = 8.47 \times 10^{22}\text{ cm}^{-3}$ corresponds to an exclusion pressure

$$P = \frac{2}{3} \frac{E_{\text{tot}}}{V} \approx \frac{2}{5} \frac{N}{V} E_F = 2.37 \times 10^{29}\text{ eV/m}^3 = 3.80 \times 10^{10}\text{ N/m}^2$$

(which is a formidable pressure, of the order of 4×10^5 atmospheres). This pressure corresponds to a small **isothermal compressibility**,

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T.$$

The inverse of of the compressibility,

$$B_{\text{el.gas}} \equiv \frac{1}{\kappa_T} = -V \left(\frac{\partial P}{\partial V} \right)_T,$$

known as the **bulk modulus**, then becomes large for the electron gas. Since P is proportional to $V^{-5/3}$, we get

$$B_{\text{el.gas}} = \frac{5}{3} P = 6.33 \times 10^{10} \text{ N/m}^2.$$

This turns out to be of the same order of magnitude as the bulk modulus of the copper metal itself, which is measured to $B_{\text{Cu}} = 13.4 \times 10^{10} \text{ N/m}^2$. [The stable ground state of the metal is the result of a complicated interplay between the exclusion pressure, which acts to *expand* the metal, the *attraction* between the gas of conduction electrons and the positively charged ions, and the “Pauli repulsion” between the conduction electrons and the electronic cloud belonging to each ion.]

Thermal properties

The free-electron-model result

$$E_{\text{tot}} \approx E_{\text{tot}}(T=0) + N \frac{\pi^2}{4} \frac{k_B^2 T^2}{E_F} \quad (k_B T \ll E_F)$$

also gives a description of the specific heat of the electron gas, which comes out as

$$C_V = \frac{\partial E_{\text{tot}}}{\partial T} = N k_B \left(\frac{1}{2} \pi^2 \frac{k_B T}{E_F} \right). \quad (\text{T8.35})$$

This is much less than the classical result, which is $3Nk_B/2$.⁴ The heat capacity C_V of the metal at normal temperatures is therefore due almost exclusively to the motion of the ions; the contribution from the conduction electrons is a factor

$$\frac{\frac{1}{2} \pi^2 k_B T / E_F}{3/2} = \frac{\pi^2}{3} \frac{k_B T}{E_F} \sim 10^{-2}$$

smaller than expected classically. Before the advent of quantum mechanics, this discrepancy between classical theory and experiments was a mystery.

⁴Each of the “free” electrons have three translational degrees of freedom. In classical statistical mechanics, one learns that the average kinetic energy for each of these degrees of freedom is $\frac{1}{2}k_B T$. This is called the equipartition principle.

Band theory of solids

(Hemmer p 213, Griffiths p 198)

The main shortcoming of this *free*-electron-gas model lies in the assumption of a *constant* potential inside the crystal. When this potential is replaced by the more realistic periodic potential mentioned above, one finds a surprising result: The allowed energies are no longer distributed continuously, but occur in **energy bands** with $2N_{\text{ion}}$ states in each band, where N_{ion} is the number of ions. Between these bands there are energy gaps with no states. (See Hemmer p 209, Griffiths p 198 and Brehm & Mullin p 596.) With this band theory of solids it is possible to explain the difference between insulators, metals and semiconductors. Band theory is a very important part of modern solid state physics.

8.2.c Electrons in a white dwarf star***⁵

(Hemmer p 196, Griffiths p 218, B&J p 484)

When the fusion processes in an ordinary star die out, and the star cools down, the interior of the star is no longer able to withstand the “gravitational pressure”, and the star may collapse to a **white dwarf**. What makes this process stop (if the stellar mass M is not too high), is the exclusion pressure from the electron gas. (There may also be other fermions present, but the electron pressure will dominate, because as we have seen, E_F and $P = \frac{2}{3} \frac{N}{V} E_F$ are inversely proportional to m .)

To understand how this works we can use a simplified model (p 218 in Griffiths) where a star of total mass M is assumed to have constant mass density. The number of nucleons with mass m_n then is $N_n \approx M/m_n$. Assuming q fermions (electrons) per nucleon, we then have a total number $N_f = qN_n$ of fermions with mass m_f (m_e) in the volume $V = \frac{4}{3}\pi R^3$. This gives a Fermi momentum

$$p_F = \frac{\hbar}{R} \left(\frac{9\pi}{4} qN_n \right)^{1/3}. \quad (\text{T8.36})$$

A non-relativistic calculation then gives a total kinetic energy $E_{\text{kin}} = \frac{3}{5} N_f E_F$ which comes out inversely proportional to the square of the stellar radius R :

$$E_{\text{kin}} = \frac{b}{R^2}, \quad \text{with} \quad b = \frac{3}{5} \left(\frac{9\pi}{4} \right)^{2/3} (qN_n)^{5/3} \frac{\hbar^2}{2m_f}. \quad (\text{T8.37})$$

It is easy to show that the total gravitational (potential) energy is

$$E_G = - \int \frac{Gm(r)dm}{r} = -G \int_0^R \frac{(\rho \cdot 4\pi r^3/3)(\rho \cdot 4\pi r^2)dr}{r} = -\frac{3}{5} \frac{GM^2}{R} \equiv -\frac{a}{R}, \quad (\text{T8.38})$$

where G is the gravitational constant. As a function of R we see that the total energy

$$E_{\text{star}} = E_{\text{kin}} + E_G = b/R^2 - a/R \quad (\text{T8.39})$$

is zero for $R = \infty$. For large decreasing R it decreases (because $E_G = -a/R$ dominates). But when R decreases further the positive term $E_{\text{kin}} = b/R^2$ will eventually make E_{star} increase again. Thus there is an energy minimum for a certain value of R , corresponding to a stable configuration. This value of R is given by

$$\frac{dE}{dR} = -\frac{2b}{R^3} + \frac{a}{R^2} = 0,$$

⁵This section is not a part of the course.

which gives a radius

$$R = \frac{2b}{a} = \left(\frac{9\pi}{4}\right)^{2/3} \frac{q^{5/3}\hbar^2}{Gm_fm_n^2} \frac{1}{N_n^{1/3}}. \quad (\text{T8.40})$$

By inserting numbers one finds that this simplified model gives a radius of the order of 10^2 – 10^3 kilometers for a white dwarf with a mass of the order of the solar mass M_\odot . More realistic models give somewhat larger radii, but still these white dwarfs are very compact objects, with very high mass densities.

In fact the density of the Fermi gas is so high that relativistic effects must be taken into account. This means that the behaviour of the function $E = E_{\text{kin}}(R) + E_G(R)$ will be modified for small R . To get an idea of what happens, we can use the ultra-relativistic energy-momentum relation $E \approx cp$. With

$$p_F = \frac{1}{R} \left(\frac{9\pi}{4} q N_n\right)^{1/3} \quad \text{and} \quad E_G = -\frac{3}{5} \frac{Gm_n^2}{R} N_n^2$$

(from the calculation above) we find that

$$E = \frac{3}{5} \frac{1}{R} \left[\hbar c \left(\frac{9\pi}{4} q^4\right)^{1/3} N_n^{4/3} - Gm_n^2 N_n^2 \right].$$

The main point here is that the kinetic term now has the same $1/R$ -behaviour as the potential term. We therefore get a minimum in the energy E (and a stable star) only if the size of the kinetic term is larger than that of E_G , making E positive for small R . This happens only if

$$N_n \leq \left[\frac{\hbar c}{Gm_n^2} \left(\frac{9\pi}{4} q^4\right)^{1/3} \right]^{3/2} \sim 2 \times 10^{57}. \quad (\text{T8.41})$$

The moral of this story is that if N_n is larger than this number, the exclusion pressure of the electron gas is unable to stop the gravitational collapse. Heavier stars than this will therefore not end up as white dwarf stars. This was shown by S. Chandrasekhar in 1934, who found the so-called **Chandrasekhar limit**,

$$M \approx 1.4(2q)^2 M_\odot.$$

The white dwarf radii for masses just below this limit turn out to be of the order of 5000 km.

A heavier star than this will continue its collapse, and the large energies released create an explosion known as a supernova. The mass remaining in the core of such a supernova will create a neutron star. The reason is that at extremely high densities **inverse beta decay**, $e^- + p \rightarrow n + \nu$, becomes energetically favourable, converting the electrons and protons into neutrons (and neutrinos, which are liberated and creates the explosion). Provided that the mass of the neutron star is not too large, the exclusion pressure of the neutron gas will prevent further collapse. Using the same formula as above for R , only with $m_f = m_n$ (instead of m_e), one finds that the radii of such neutron stars are a factor ~ 2000 smaller than for a white dwarf, that is, only a few kilometers. The density of neutron stars is then somewhat larger than for nuclei, of the order of 10^{44} nucleons per m^3 , or 10^{15} g/cm^3 . Although the neutron stars may have temperatures of the order of 10^9 K, they still are “cold” systems, because at these densities the Fermi temperatures are much higher, $\sim 10^{11}$ K.

But again, if the mass is too big, the neutrons “go relativistic”, and then the neutron star may collapse to a **black hole**. The mass limit is believed to be around $3M_\odot$. This limit requires detailed calculations involving general relativity theory. It is also necessary to leave the ideal-gas approximation and take into account the interactions between the nucleons.

8.2.d Fermi gas model for nuclei

(B&J p 510, Brehm & Mullin p 695)

The nucleons (protons and neutrons) in a nucleus are held together by the **strong** but very short-range nucleon-nucleon force. This attractive force is much stronger than the electromagnetic repulsion between the protons, and is counterbalanced mainly by the exclusion pressures from the protons and neutrons. The total binding energy of a nucleus is roughly proportional to the **nucleon number** A , and the **nuclear radius** R goes as

$$R \approx R_0 A^{1/3}, \quad \text{where } R_0 \approx 1.07 \text{ fm.}$$

This means that the nuclear volume is proportional to A ,

$$V = \frac{4}{3}\pi R^3 \approx A \cdot \frac{4}{3}\pi R_0^3.$$

Thus each nucleon occupies roughly the same volume $\frac{4}{3}\pi R_0^3$ in all nuclei. To account for these facts it turns out that one has to assume that the nucleon-nucleon force is strongly repulsive for short distances, $r \leq 0.4\text{--}0.5$ fm. (See B&J p 507, or Brehm & Mullin, section 14-1.)



The almost constant density of nucleons sometimes make us picture the nucleus as a collection of close-packed “balls”, each ball representing a nucleon, and one might be tempted to think of an almost static structure, but of course such a picture is highly misleading: The nucleons are definitely not static, as we know already from the uncertainty principle.

To get an idea about their motion we may use the simple **Fermi gas model for nuclei**. This model treats the Z protons and the N neutrons as ideal Fermi gases contained within the nuclear volume, which acts as a spherical potential well of depth ~ 50 MeV. With $V = A \cdot \frac{4}{3}\pi R_0^3$ we find a Fermi momentum for the proton gas given by

$$p_F^{(p)} = \hbar \left(3\pi^2 \frac{Z}{V} \right)^{1/3} = \frac{\hbar}{R_0} \left(\frac{9\pi}{4} \frac{Z}{A} \right)^{1/3}, \quad (A = Z + N) \quad (\text{T8.42})$$

and similarly for the neutrons. The two Fermi energies then are

$$E_F^{(p)} = \frac{\hbar^2}{2MR_0^2} \left(\frac{9\pi}{4} \frac{Z}{A} \right)^{2/3} \quad \text{and} \quad E_F^{(n)} = \frac{\hbar^2}{2MR_0^2} \left(\frac{9\pi}{4} \frac{N}{A} \right)^{2/3}. \quad (\text{T8.43})$$

With $M \approx 939$ MeV/ $c^2 \approx 940 m_e$, $R_0 \approx 1.07$ fm and $N/A \sim Z/A \sim 1/2$ we find that these energies are approximately

$$E_F^{(p)} \approx E_F^{(n)} \approx 43 \text{ MeV.}$$

This shows that the nucleons have speeds of the order of

$$v = c \sqrt{\frac{2E}{Mc^2}} \sim c \sqrt{1/20} \sim 0.2 c,$$

so that it is reasonably correct to treat them non-relativistically, but they are definitely moving around.

This simplified model also explains why the most stable nuclei prefer to have $N \sim Z$. (This holds mainly for light nuclei. For heavier ones there is a preference of larger N than Z . But that is due to the Coulomb repulsion between the protons, which so far has been disregarded; we are neglecting all interactions between the nucleons.)

From the expressions above it follows that the total kinetic energy is

$$E_{\text{kin}} = \frac{3}{5}Z \cdot E_F^{(p)} + \frac{3}{5}N \cdot E_F^{(n)} = k[(Z/A)^{5/3} + (N/A)^{5/3}],$$

with

$$k \equiv \frac{3}{5}A \cdot \frac{\hbar^2}{2MR_0^2} \left(\frac{9\pi}{4}\right)^{2/3}, \quad \text{and} \quad N = A - Z.$$

A nucleus can “transform” neutrons into protons or vice versa via β decay or inverse β decay. (See Brehm and Mullin, p692 and p 761.) Therefore, it is relevant to keep the nucleon number $A = Z + N$ fixed, while we vary Z and $N = A - Z$ to find the minimum of the above expression for E_{kin} . It is easy to see that this sum is minimal for $Z = N = A/2$. Introducing $Z = \frac{1}{2}A - x$ and $N = \frac{1}{2}A + x$, and using the binomial expansion, we have

$$\begin{aligned} \left(\frac{Z}{A}\right)^{5/3} &= \left(\frac{1}{2}\right)^{5/3} \left(1 - \frac{2x}{A}\right)^{5/3} = \left(\frac{1}{2}\right)^{5/3} \left(1 - \frac{10x}{3A} + \frac{20x^2}{9A^2} + \dots\right), \\ \left(\frac{N}{A}\right)^{5/3} &= \left(\frac{1}{2}\right)^{5/3} \left(1 + \frac{2x}{A}\right)^{5/3} = \left(\frac{1}{2}\right)^{5/3} \left(1 + \frac{10x}{3A} + \frac{20x^2}{9A^2} + \dots\right), \end{aligned}$$

It follows that

$$E_{\text{kin}} \approx \frac{3}{20}(9\pi)^{2/3} \frac{\hbar^2}{2MR_0^2} \frac{1}{A} \left[1 + \frac{20}{9}\left(\frac{1}{2}A - Z\right)^2\right],$$

which is minimal for $Z = N = \frac{1}{2}A$, q.e.d. The second-order term in this expression goes as

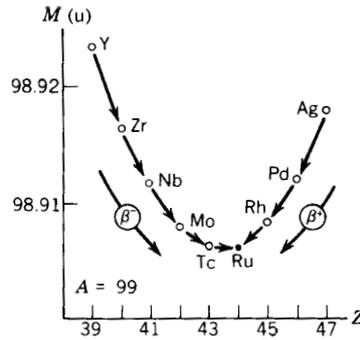
$$\frac{(9\pi)^{2/3}}{6} \frac{\hbar^2}{MR_0^2} \frac{(\frac{1}{2}A - Z)^2}{A},$$

and gives a qualitative explanation of the so-called **symmetry term** in the following empirical formula for atomic masses

$$\begin{aligned} M(^A\text{X}) &= Z M(^1\text{H}) + (A - Z)M_n \\ &- \left[a_1 A - a_2 A^{2/3} - a_3 \frac{Z^2}{A^{1/3}} - a_4 \frac{(\frac{1}{2}A - Z)^2}{A} + \epsilon_5 \right] / c^2. \end{aligned} \quad (\text{T8.44})$$

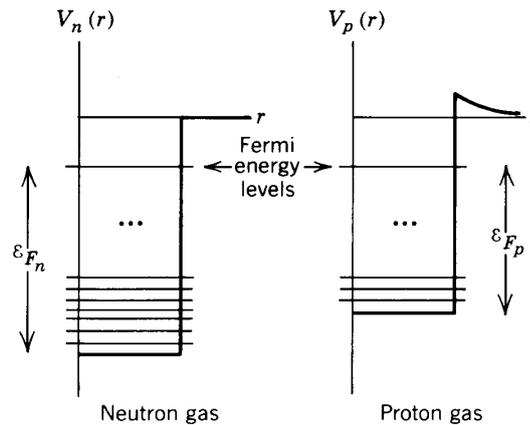
(See Brehm & Mullin pp 691–699.) Here, the square bracket represents the total binding energy of the nucleus. We see that the fourth term in this empirical formula is precisely of second order in $\frac{1}{2}A - Z$, as found in our model. Thus the simple model of two ideal Fermi gases gives a theoretical explanation of this empirical term. The *third* empirical term takes into account the Coulomb repulsion between the protons. Also this term can be explained theoretically; the calculation is analogous to the calculation of the gravitational energy in (T8.38).

Taken together, the symmetry term and the Coulomb term predict that the most stable **isobar** (for a fixed A) will have N somewhat larger than Z , particularly for large A . An example is ${}^{238}_{92}\text{U}$. The figure shows isobars for $A = 99$.



Note as mentioned above that a nucleus can transform into another isobar via β decay or inverse β decay. (See BM pp 692 and 761.)

The Coulomb repulsion term can be included into the fermi gas model by shifting the potential well for the protons upwards. For the most stable isobar, the Fermi levels for protons and neutrons then are at the same height, as shown in the figure below on the right. In this situation the (kinetic) Fermi energy of the neutrons is higher than that of the protons, consistent with N being larger than Z . With this modification, the simple Fermi model of the nucleus is able to explain at least qualitatively why the number of neutrons tends to exceed that of protons in the most stable nuclei.



8.3 Ideal boson gas

8.3.a The Bose–Einstein distribution

(Griffiths p 214, Brehm & Mullin p 552)

Pauli’s exclusion principle is (as we remember) a consequence of the experimental fact that identical fermions (particles with spin $1/2$, $3/2$, $5/2$ etc) require wave functions which are *antisymmetric* with respect to the interchange of any pair of particle indices. Such a wave function can be written as a determinant, and we remember that this determinant is equal to zero if we try to put more than one fermion into the same one-particle state. (See Hemmer p 189–192 or Griffiths p 179 for a reminder.)

We also remember that for identical bosons (particles with spin 0, 1, 2, etc) Nature requires wave functions that are *symmetric* with respect to interchange of any pair of particles. Then there is nothing stopping us from putting more than one boson into the same state. On the contrary, bosons in a way *prefer* to be in the same state. We shall here briefly explain how this comes about.

According to **quantum statistical mechanics**, when a system of identical bosons is in equilibrium at a temperature T , the average (or expected) number of particles (occupation number) in a one-particle state with energy E is given by the **Bose–Einstein distribution**,

$$\boxed{\langle n \rangle = \frac{1}{e^{(E-\mu)/k_B T} - 1}} \quad \left(\begin{array}{l} \text{Bose–Einstein} \\ \text{distribution} \end{array} \right) \quad (\text{T8.45})$$

Formally, this formula differs from the the Fermi–Dirac formula only by sign of the last term in the denominator. This sign, however, is very important: It means, e.g., that the occupation number becomes larger than 1 for

$$(E - \mu)/k_B T < \ln 2.$$

Here, μ is again the **chemical potential**. For systems where the number N of bosons is conserved (as for example for a gas of helium-4 atoms in a volume V), the chemical potential $\mu(T)$ is implicitly determined by the relation

$$N = \int_0^\infty \frac{g(E)dE}{e^{(E-\mu)/k_B T} - 1}. \quad (\text{T8.46})$$

Here, as in the corresponding relation (T8.29) for fermions, $g(E)$ is the *density of states*, $g(E)dE$ is the number of *states* in the energy interval $(E, E + dE)$, and the integrand is the expected number of bosons with energies in the interval $(E, E + dE)$. Also for bosons, the chemical potential will depend on the temperature (and on the other parameters).

For the massless photons the number is *not* conserved (it increases with T), and in statistical mechanics one then learns that $\mu = 0$. (See Griffiths p 216.) Thus if we consider a wave mode with frequency ν and one of the two possible polarizations — or as we put it in quantum mechanics — a mode with energy $E = h\nu$ — Bose–Einstein’s distribution law states that the expected number of photons (the occupation number) in this mode is

$$\boxed{\langle n \rangle_{\text{f}} = \frac{1}{e^{h\nu/k_B T} - 1}} \quad (\text{photons}) \quad (\text{T8.47})$$

8.3.b The Maxwell–Boltzmann distribution

We shall return to the photons, but first a little digression. If a gas of bosons or fermions is heated to very high temperatures, we can all imagine that most of the particles get excited to high energies. Then the particles can choose between a very large number of available states. This means that the average number of particles in each state, that is, the occupation number

$$\langle n \rangle = \frac{1}{e^{(E-\mu)/k_B T} \mp 1} \quad (\text{T8.48})$$

for most of the occupied levels tends to decrease with increasing temperature, so that all the occupation numbers are much smaller than 1. Then the exponentials in the denominators are much larger than 1, and

$$\boxed{\langle n \rangle \approx e^{-(E-\mu)/k_B T}} \quad \left(\begin{array}{l} \text{Maxwell–Boltzmann's} \\ \text{distribution law} \end{array} \right) \quad (\text{T8.49})$$

This is the **Maxwell–Boltzmann distribution**. The *moral* is that for high temperatures (or dilute gases), it doesn't matter much whether the particles are fermions or bosons. Historically the Maxwell–Boltzmann distribution was proposed long before quantum mechanics; it can be derived classically, assuming that the particles are distinguishable.

Here we note the following important point: If we compare two one-particle states a and b , it follows that the ratio between the occupation numbers is

$$\frac{\langle n \rangle_b}{\langle n \rangle_a} = e^{-(E_b - E_a)/k_B T}. \quad (\text{T8.50})$$

favouring the state with the lowest energy, when the system is at equilibrium at the temperature T . The factor on the right is called a Boltzmann factor, and in a way is classical statistical mechanics in a nut-shell.

8.3.c Planck's radiation law

Let us now return to the photons. Because the electromagnetic waves in a cavity satisfy essentially the same boundary conditions as the de Broglie waves, we may state that the number of electromagnetic *modes* in the phase space element $V d^3 p$ is given by (T8.11), multiplied by a factor 2 counting the two orthogonal polarizations:

$$dN = 2 \frac{V d^3 p}{h^3}.$$

With $d^3 p = 4\pi p^2 dp$ and $p = E/c = h\nu/c$ it follows that the number of modes in the frequency interval $(\nu, \nu + d\nu)$ is

$$dN = \frac{8\pi V}{c^3} \nu^2 d\nu, \quad (\text{T8.51})$$

as was also shown on page 8. The number of photons in each mode is given by (T8.47). The number of photons in the interval $(\nu, \nu + d\nu)$ therefore is

$$n(\nu) d\nu = \frac{8\pi V}{c^3} \frac{\nu^2 d\nu}{e^{h\nu/k_B T} - 1}. \quad (\text{T8.52})$$

Multiplying with the photon energy $h\nu$ and dividing with the volume V , we find the *energy density* (energy per unit volume) in the frequency range $d\nu$:

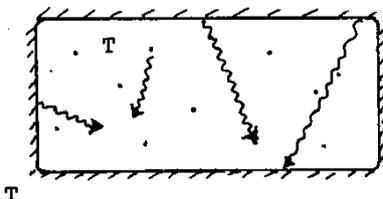
$$\boxed{u(\nu)d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{e^{h\nu/k_B T} - 1}} \quad \left(\begin{array}{l} \text{Planck's} \\ \text{radiation law} \end{array} \right) \quad (\text{T8.53})$$

This is **Planck's radiation law**, in which Planck's constant h was first introduced, and which in a way was the start of quantum mechanics. (See Hemmer p 9.)

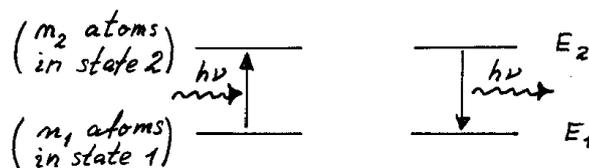
8.3.d Einstein's A and B coefficients

(Griffiths p 311, Brehm & Mullin p 170)

The figure shows a box containing both photons and a number of atoms of a certain kind, in equilibrium at temperature T .



Even if the system is in equilibrium, photons are constantly being absorbed and emitted by the walls, and also by atoms which are excited or de-excited. Let us consider two particular states ψ_1 and ψ_2 for the atoms with energies E_1 and E_2 and let n_1 and n_2 be the number of atoms in the respective states. For simplicity, we refer to the two states as state 1 and state 2. These have been chosen such that atoms can “jump” between state 1 and 2 by emission or absorption of a photon with energy $h\nu = E_2 - E_1$.



The numbers n_1 and n_2 will in general fluctuate, but when the system is in equilibrium, the ratio between n_2 and n_1 is very accurately determined by the Boltzmann factor

$$\frac{n_2}{n_1} = e^{-(E_2 - E_1)/k_B T} = e^{-h\nu/k_B T}. \quad (\text{T8.54})$$

We also note that the energy density (per unit frequency) of the photons with frequency ν is given by

$$u(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1} \equiv \frac{8\pi h\nu^3}{c^3} \langle n \rangle_{ph}, \quad (\text{T8.55})$$

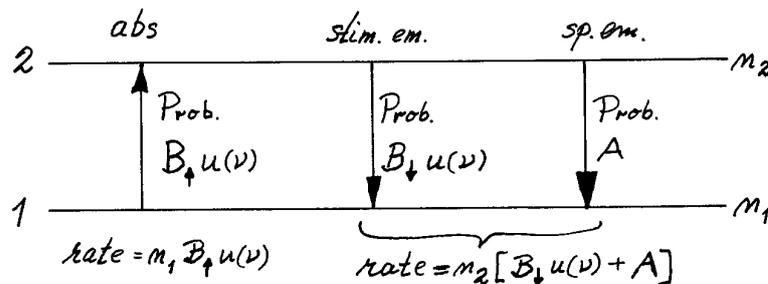
according to Planck's law.

Even at equilibrium there is an ongoing “transport” of atoms up and down between the two states: Photons with frequency ν will excite *some* of the atoms from state 1 to state

2. The probability (per unit time) that an atom in state 1 absorbs a photon with frequency ν must be proportional to the chance to meet such a photon, that is to the energy density $u(\nu)$:

$$P_{\text{abs}} = B_{\uparrow} u(\nu), \quad (\text{T8.56})$$

where B_{\uparrow} is a proportionality constant. The number excited per unit time (rate) then is $n_1 P_{\text{abs}} = n_1 B_{\uparrow} u(\nu)$:



This rate adds to the population n_2 in state 2. At the same time there is a probability (per unit time)

$$P_{\text{sp.em}} = A$$

of **spontaneous emission**, which *reduces* n_2 by a rate $n_2 A$. This emission is called spontaneous because the probability is independent of $u(\nu)$. Therefore, this rate can not counter balance the rate $n_1 P_{\text{abs}}$.

Einstein, who established this argument and introduced the A and B coefficients, therefore had to invent another contribution, the so-called **stimulated emission**. The stimulation comes from the photons with frequency ν . Therefore, Einstein had to assume that the probability (per unit time) of stimulated emission must be proportional to $u(\nu)$:

$$P_{\text{st.em}} = B_{\downarrow} u(\nu), \quad (\text{T8.57})$$

introducing a third coefficient B_{\downarrow} . This should give a rate $n_2 B_{\downarrow} u(\nu)$ of de-excited atoms. This was a surprising result in 1917: Disturbing the atoms with radiation not only makes them *absorb* photons; it even makes some of them *emit* radiation.

To see how Einstein arrived at this result, we collect the three contributions, and find that the rate of change of n_2 is

$$\frac{dn_2}{dt} = n_1 B_{\uparrow} u(\nu) - n_2 (B_{\downarrow} u(\nu) + A).$$

At equilibrium, both n_1 and n_2 must stay constant, except for fluctuations. Thus we obtain the relation

$$n_1 B_{\uparrow} u(\nu) = n_2 (B_{\downarrow} u(\nu) + A),$$

showing that the three Einstein coefficients are not independent. Solving for $u(\nu)$, and using the ratio for n_2/n_1 given by the Boltzmann factor above, we have

$$u(\nu) = \frac{A}{B_{\downarrow}} \frac{1}{(B_{\uparrow}/B_{\downarrow}) e^{h\nu/k_B T} - 1}.$$

Still following Einstein we may compare with Planck's radiation law given above, in (T8.55). The conclusion is that the two B coefficients have to be equal, while A/B comes out proportional to the third power of the frequency:

$$\boxed{\begin{aligned} B_{\uparrow} &= B_{\downarrow} \equiv B, \\ \frac{A}{B} &= \frac{8\pi h\nu^3}{c^3} = \frac{u(\nu)}{\langle n \rangle_{\text{f}}}. \end{aligned}} \quad \left(\begin{array}{l} \text{the Einstein} \\ \text{coefficients} \end{array} \right) \quad (\text{T8.58})$$

In this way Einstein was able to show that the probabilities (per unit time) for absorption and stimulated emission are equal, $Bu(\nu)$.

From the second relation we note that the ratio between the probabilities for *stimulated* emission and *spontaneous* emission is equal to the occupation number:

$$\frac{P_{\text{st.em}}}{P_{\text{sp.em}}} = \frac{Bu(\nu)}{A} = \langle n \rangle_{\text{ph}} = \frac{1}{e^{h\nu/k_B T} - 1}. \quad (\text{T8.59})$$

This result may be illustrated by two examples:

(i) Suppose that we have an excited atom in a box at room temperature ($k_B T \sim 0.025$ eV) and consider an optical transition, corresponding to emission of a photon in the visible region, with $h\nu \sim 2$ eV. Then $h\nu/k_B T \sim 80$, and the relevant occupation numbers $\langle n \rangle_{\text{f}} \approx e^{-h\nu/k_B T} \sim e^{-80}$ are so small that the probability of stimulated emission is non-existing. Emission must then occur spontaneously.

(ii) On the other hand, if we consider a transition in the microwave region, then we have $h\nu/k_B T \sim 10^{-4}/0.025 \sim 1/250$, and the occupation numbers become very large

$$\langle n \rangle_{\text{f}} = \frac{1}{e^{h\nu/k_B T} - 1} \approx \frac{k_B T}{h\nu} \sim 250.$$

In such cases stimulated emission will dominate strongly over the spontaneous process.

The relations (T8.58) were discovered by Einstein already in 1917. After the development of quantum mechanics and quantum electrodynamics, Einstein's relations could be verified and the coefficients could be *calculated* (not only the ratios between them). It turns out that the spontaneous emission rate is

$$A = \alpha \frac{4\omega^3}{3c^2} |\mathbf{d}|^2, \quad (\text{T8.60})$$

where $\omega = 2\pi\nu$, α is the fine-structure constant and \mathbf{d} is the so-called **dipole moment** of the transition,

$$\mathbf{d} = \int \psi_2^* \mathbf{r} \psi_1 d^3r. \quad (\text{T8.61})$$

This result is valid in the so-called **dipole approximation**, which requires that the photon wave number times the "size" R of the states, kR , is much smaller than 1, corresponding to $\lambda \gg R$. This is reasonably well satisfied for most atomic transitions.

Quantum electrodynamics verifies Einstein's results from 1917: When photons of frequency ν are already present, spontaneous emission is supplemented by stimulated or induced emission. It turns out that the total probability (w_{em}) per unit time for emission into a mode which already contains n photons is given by a formula containing a proportionality

factor $n + 1$. For $n = 0$, this formula describes spontaneous emission. This means that the total emission probability is a factor $n + 1$ times the spontaneous probability,

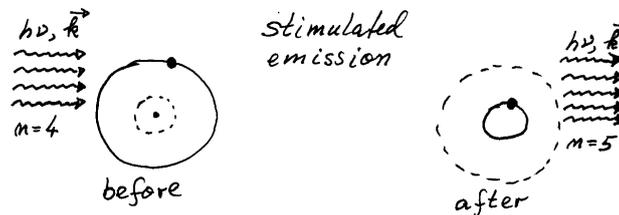
$$w_{\text{em}} = (n + 1)w_{\text{sp}}.$$

The probability for stimulated emission, which is the difference between these, then becomes

$$w_{\text{stim}} \equiv w_{\text{em}} - w_{\text{sp}} = nw_{\text{sp}}, \quad (\text{T8.62})$$

in agreement with (T8.59).

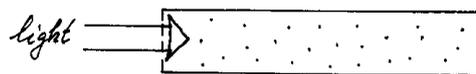
The moral is that when an excited atom is ready to emit a photon, the process happens much faster in the presence of suitable electromagnetic modes with large numbers of photons. The photons (and other bosons) are “sociable”; given a choice they will prefer the mode (state) with the largest occupation number n .



8.3.e Masers and lasers

(B&J p 735, avsn. 3-9 in Brehm & Mullin)

MASER is an acronym for Microwave Amplification by Stimulated Emission of Radiation. LASER is the same thing with Light instead of Microwave. Both these devices utilize stimulated emission from excited atoms or molecules.



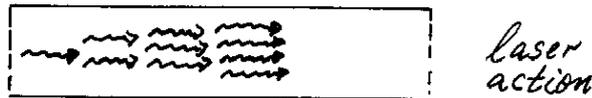
Let us imagine a container with atoms, which is subjected to a beam of light, with a frequency ν corresponding to the energy difference between the states 1 and 2. The photon modes (\mathbf{k}_i) which are represented in such a beam can have much higher occupation numbers than the equilibrium value

$$\langle n \rangle_{ph} = \frac{1}{e^{h\nu/k_B T} - 1},$$

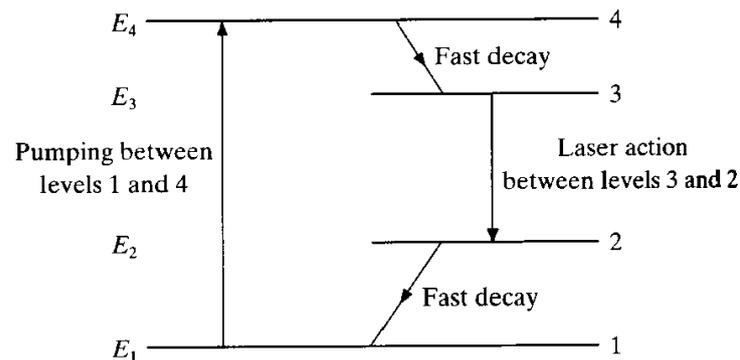
which is otherwise typical in the container. (The total system, including the beam, is of course no longer in equilibrium.)

The question then is: Will the light beam be amplified or not? We first note that photons which are emitted spontaneously will be distributed isotropically, and therefore give a negligible contribution to the beam. Since the probabilities for absorption and stimulated emission are equal, and n_2 normally is smaller than n_1 , we can conclude that the number of photons emitted “into” the beam will be smaller than the number absorbed. The beam will therefore lose intensity.

But this argument also tells us what is needed to get amplification: In some way or other we must bring the collection of atoms out of equilibrium, such that n_2 becomes larger than n_1 . This is called **population inversion**.



To make a laser or a maser therefore means to invent some mechanism to create population inversion for two chosen levels. The figure illustrates the principle of the so-called four-level laser, with $E_1 < E_2 < E_3 < E_4$.



Principle of the four-level laser.

Using a suitable “pumping” mechanism⁶ one can raise the atoms from the ground state 1 to level 4. This level is chosen such that it has a fast spontaneous decay to level 3, which is more long-lived. If the decay from 2 to 1 is also fast, one can obtain population inversion between levels 3 and 2, such that laser action with stimulated emission occurs between 3 and 2. By a mirror arrangement one can obtain strong amplification in closely spaced optical modes with almost parallel wave vectors \mathbf{k} . This way it is possible to produce highly monochromatic and coherent light. (See section 3-9 in Brehm & Mullin.)

⁶Pumping can be obtained for example by using electrical discharge or by using a lamp of sufficient intensity.