Chapter 10
Fermi and Bose gases

10.1 Fermi-Dirac and Bose-Einstein distribution

When we discussed the ideal gas we assumed that quantum effects were not important. This was implied when we introduced the term $1/N!$ for the partition function for the ideal gas, because this term only was valid in the limit when the number of states are many compared to the number of particles.

Now, we will address the general case of a quantum gas. The concepts and methods we introduce here will be important for your understanding of applied problems in quantum mechanics, such as electrical conducitivity, solar power cells, thermoelectric materials, neutron stars, and many other processes.

The system we will study is a system of non-interacting particles in a box of size $L \times L \times L = V$. For a single particle in a box, we know that the possible translational states of the particle have energies

$$
\begin{aligned}
\varepsilon(n_x, n_y, n_z) &= \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right) \\
&= a \left(n_x^2 + n_y^2 + n_z^2\right) = an^2 ,
\end{aligned}
\tag{10.1}
$$

where

$$
a = \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 = \frac{h^2}{8mV^{2/3}} ,
\tag{10.2}
$$

and m is the mass of the particle. The three positive integers n_x, n_y, n_z enumerates all the possible states of the system. That is, the state of one particle in a box is given by (n_x, n_y, n_z), where $n_x = 0, 1, 2, \ldots$, $n_y = 0, 1, 2, \ldots$, $n_z = 0, 1, 2, \ldots$.

This describes a the states of a single particle in a box. However, if we have many particles in the same box, we need to address whether two particles can occupy the same quantum state in the system. This depends on the type of particle:

- For **Fermions** (1/2 spin) Only 0 or 1 fermion can be in a particular state.
- For **Bosons** (integer spin) Any number of bosons can be in a particular state.

Given this condition, we will assume that there are no other interactions between the particles and that they can occupy any of the possible quantum states of the system.

How can we find the thermodynamics of this system using a statistical physics approach? We will apply a simplification that allows us to address each state separately: Let us assume that we study a grand-canonical system, that is, we will assume a system at constant temperature, T, volume, V, and chemical potential μ. We will then use a "trick" – we will look only at a single state in the system, find the probability that this state is occupied, and then sum the occupation numbers of all states to find the total number of particles in the system and the total energy of the system.

Let us first look at a system of Fermions with spin $1/2$, such as the electrons in an electron gas. In this case, there can only be one particle in each state. However, for each translational state given by (n_x, n_y, n_z) we will have 2 spin states, $\sigma = \pm 1/2$. Let us pick one such state, (n_x, n_y, n_z, σ) with energy $\varepsilon(n_x, n_y, n_z)$ (For example, the state $(1, 0, 1, -1/2)$ with energy $\varepsilon = a(1^2 + 0^2 + 1^2) = 2a$). We study the occupancy of this state using the Gibbs sum approach. The Gibbs sum is the sum over the possible number of particles in this state, and for each number of particles, we sum over all the possible states of the system given this number of particles. In this case these sums are simple. The system may have either $N = 0$ particles or $N = 1$ particle. For $N = 0$ the system consisting of the state (n_x, n_y, n_z, σ) can only have one possible energy – zero. For $N = 1$, the energy of the system is simply $\varepsilon(n_x, n_y, n_z, \sigma)$, which we write at ε for short. The Gibbs sum is therefore

$$
\begin{aligned}
Z_G &= \sum_{N=0}^{1} \sum_{s(N)} e^{-(\varepsilon_{s(N)} - N\mu)/kT} \\
&= e^{-(0 - 0\mu)/kT} + e^{-(\varepsilon - 1\mu)/kT} \\
&= 1 + e^{-(\varepsilon - \mu)/kT} \ .
\end{aligned}
\tag{10.3}
$$

In the Gibbs sum formalism, the probability to have N particles in the system and for the system to be in the state $s(N)$ is

$$
P(\varepsilon_{s(N)}, N) = \frac{1}{Z_G} e^{-(\varepsilon_{s(N)} - N\mu)/kT} \ .,
\tag{10.4}
$$

The average number of particles in the state $s = (n_x, n_y, n_z, \sigma)$, $\bar{N}_s$ is then

$$
\begin{aligned}
\bar{N}_{(n_x, n_y, n_z, \sigma)} &= \sum_{N=0}^{1} P(\varepsilon_{s(N)}, N) N \\
&= 0 \cdot 1 + 1 \cdot \frac{1}{Z_G} e^{-(\varepsilon - \mu)/kT} \\
&= \frac{e^{-(\varepsilon - \mu)/kT}}{e^{-(\varepsilon - \mu)/kT} + 1} \\
&= \frac{1}{e^{(\varepsilon - \mu)/kT} + 1} \ .
\end{aligned}
\tag{10.5}
$$

This quantity – the average number of particles in a state (n_x, n_y, n_z, σ) – is called the **Fermi-Dirac distribution function**:

$$\bar{N}_{(n_x, n_y, n_z, \sigma)} = f_{FD}(\varepsilon; \mu, T) = \frac{1}{e^{(\varepsilon - \mu)/kT} + 1} \ . \tag{10.6}$$

Because the average number of particles in a state (n_x, n_y, n_z, σ) only depends on the energy of this state, and not on any other details of the state, we write the average number as a function of the energy ε of the state alone.

What does the average number of particles – the Fermi-Dirac distribution function – look like? First, let us look at the functional form. We see that if we introduce $x = (\varepsilon - \mu)/kT$, the functional form is

$$f(x) = \frac{1}{e^x + 1} \ , \tag{10.7}$$

This is a function that provides a smooth transition from a value of 1 when $x \ll -1$ to 0 when $x \gg +1$. We have plotted $f_{FD}(\varepsilon; \mu, T)$ as a function of $(\varepsilon - \mu)/kT$ in fig. 10.1. The temperature effectively determines the range of the transition region. We can illustrate this by introducing an energy scale in the plot. Let us use the chemical potential μ as the energy scale[1], that is, we plot $f_{FD}(\varepsilon; \mu, T)$ as a function of ε/μ for different values of T corresponding to $kT = 0.2\mu$, $kT = \mu$ and $kT = 5\mu$. We see that when the temperature goes towards zero, the function approximates a step function, and when the temperature increases the transition becomes broader. These plots were generated by the following short script:

```
% Figure a
subplot(2,1,1)
x = linspace(-10,10);
f = 1.0./(exp(x)+1);
plot(x,f)
xlabel('(\epsilon-\mu)/kT');
ylabel('f(\epsilon;\mu,T)')
% Figure b
ktvalues = [5.0 1.0 0.2];
legarray = [];
subplot(2,1,2)
for i = 1:length(ktvalues)
    kt = ktvalues(i);
    x = linspace(-20,20);
    f = 1.0./(exp((x-1)/kt)+1);
    plot(x,f); hold all
    legarray = [legarray; sprintf('$kT=%3.1f\\cdot \\epsilon$',kt)];
end
xlabel('$\epsilon/\mu$');
ylabel('$f(\epsilon, \mu,T)$')
legend(legarray);
```

---

[1]Notice that here the chemical potential is a given, constant, whereas further on, we will assume that the number of particles is constant instead, and the calculate a chemical potential that will depend on T, V, and N.
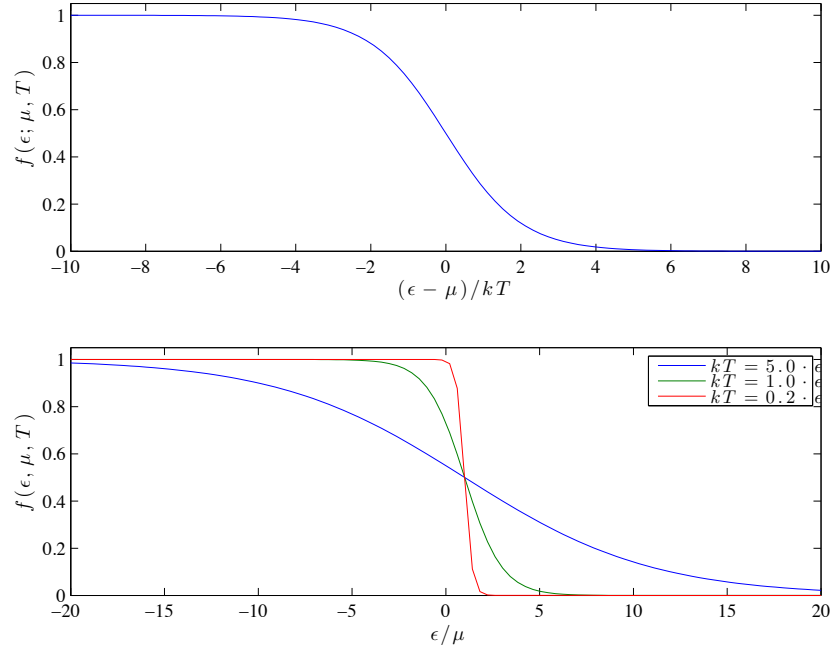
Fig. 10.1 Plot of Fermi-Dirac distribution.

What happens when $T = 0$? We see from the plots that the function approaches a step function that goes from 1 to 0 at the chemical potential. We call the chemical potential at $T = 0$ the **Fermi energy**:

$$\varepsilon_F = \mu(T = 0) . \tag{10.8}$$

At $T = 0$ all the states up to the level ε_F are occupied – and none of the levels above ε_F are occupied. Later on we will see how we can relate ε_F to the number of particles N in the gas.

10.1.1 Bose-Einstein distribution

Bosons are particles of integer spins. For Bosons, more than one particle can be in the same state. Examples of bosons are photons, phonos, and particles such as Helium-4. The Gibbs sum and the average number of particles per state is different for Bosons than for Fermions because there is no limit on the number of particles in a given state for Bosons. This means that the number of particles, N, may run from 0 to ∞. The energy $\varepsilon_{s(N)}$ of the system when there are N particles in a state s (where each particle has an energy ε_s) is $N\varepsilon_s$. The Gibbs sum is therefore

$$Z_G = \sum_{N=0}^{\infty} \sum_{s(N)} e^{-(\varepsilon_{s(N)} - N\mu)/kT}$$

$$= \sum_{N=0}^{\infty} e^{-(N\varepsilon_s - N\mu)/kT} \tag{10.9}$$

$$= \sum_{N=0}^{\infty} e^{-N(\varepsilon_s - \mu)/kT} = \frac{1}{1 - e^{-(\varepsilon_s - \mu)/kT}} \ ,$$

where the sum is the well-known geometric series. The average number of particles in state s is

$$\bar{N}_s = \sum_{N} \sum_{s(N)} \frac{N}{Z_G} e^{-(\varepsilon_{s(N)} - N\mu)/kT}$$

$$= \frac{1}{Z_G} \sum_{N} N e^{-(N\varepsilon_s - N\mu)/kT}$$

$$= \frac{1}{Z_G} \sum_{N} N e^{-N(\varepsilon_s - \mu)/kT} \tag{10.10}$$

$$= \frac{1}{Z_G} \sum_{N} kT \frac{\partial}{\partial \mu} e^{-(\varepsilon_s - \mu)N/kT}$$

$$= \frac{\partial}{\partial \mu} kT \ln Z_G \ ,$$

where we have used a usual "trick" by introducing the derivative and taking it outside the sum. The result is

$$\bar{N}_s = f_{BE}(\varepsilon_s; \mu, T) = \frac{1}{e^{(\varepsilon_s - \mu)/kT} - 1} \ . \tag{10.11}$$

Because the distribution only depends on the energy ε_s of the state s of the particle-in-box system, it is common to simply write the distribution is a function of ε. We have plotted the Bose-Einstein distribution along with the Fermi-Dirac distribution in figure 10.2.

```
% Plot FD
kt = 1.0;
legarray = [];
x = linspace(-10,10);
f = 1.0./(exp(x/kt)+1);
plot(x,f)
hold all
legarray = [legarray; 'FD'];
x = linspace(0.4,10);
f = 1.0./(exp(x/kt)-1);
plot(x,f)
legarray = [legarray; 'BE'];
x = linspace(-1.0,10);
f = exp(-x/kt);
plot(x,f)
```

```
legarray = [legarray; 'C '];
xlabel('(\epsilon-\mu)/kT');
ylabel('f(\epsilon, \mu,T)')
legend(legarray);
ax = axis();
ax(4) = 2.0;
axis(ax);
```
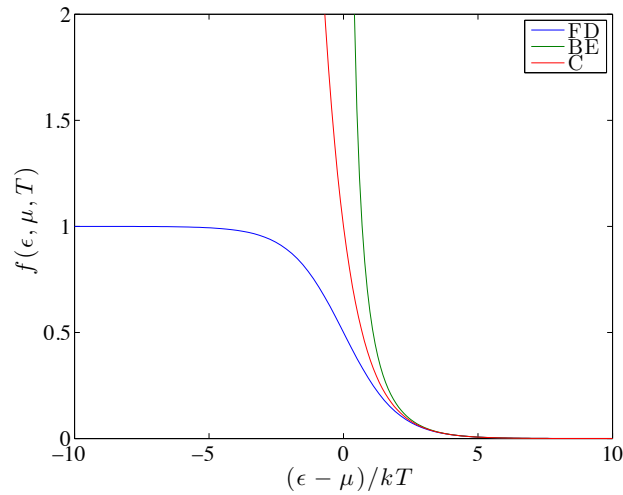

Fig. 10.2 Plot of Bose-Einstein distribution.

We see that the distribution diverges as ε approaches μ, that is, as $\varepsilon - \mu$ approaches 0. This means that as the temperature goes towards zero, all the particles will be in the ground state.

10.1.2 Classical limit

A gas is in the classical limit when the number of particles in a given state is much smaller than one. For a gas at room temperature and atmospheric pressure, the typical number of particles in each state is less than 10^{-6}. In this case, the differences between Fermions and Bosons are not important – these differences are only important when the number of particles is one or larger This means that the distribution function $f(\varepsilon; \mu, T)$, which gives the number of particles in a state with energy ε, also must be very small, $f \ll 1$. This implies that the exponential term must be very large. In that case, we can assume that it is much larger than 1 and the ± 1 in the denominator does not matter. In the classical limit we therefore get that the behavior of a Boson gas and a Fermion gas are identical. The **classical distribution function** is

$$f_{\text{classical}}(\varepsilon, \mu, T) \simeq e^{(\varepsilon - \mu)/kT} \, , \tag{10.12}$$

We have plotted all the distributions functions in the same plot in fig. 10.2, where we see that all the distribution functions are indistinguishable for large values of $(\varepsilon - \mu)/kT$.

Let us now compare this result with our results for a classical ideal gas in a canonical system, where the chemical potential is a function of T, V, N: $\mu = \mu(T, V, N)$. Since we have now addressed the system using the Gibbs formalism, the (average) number of particles in the system is a function of T, V, and μ, $\bar{N} = \bar{N}(T, V, \mu)$. How can we compare the two results? We can calculate the average total number of particles, $\bar{N}$, as a function of the chemical potential in the T, V, μ system, and then solve the resulting equation to find the chemical potential as a function of the average total number of particles. (We may not always be able to solve this equation analytically, but we may then resort to numerical methods and still save the day).

For a given chemical potential, μ, the total average number of particles, $\bar{N}$, is the sum of the average number of particles in each state, s, summed over all possible states s:

$$\bar{N} = \sum_s \bar{N}_s = \sum_s f(\varepsilon_s, \mu, T) \, , \tag{10.13}$$

In the classical limit, we have argued that the distribution function $f(\varepsilon; \mu, T)$ has a simple form, so that the sum is:

$$\bar{N} = \sum_s \exp((\varepsilon_s - \mu)/kT = e^{\mu/kT} \sum_s e^{\varepsilon_s/kT} \, . \tag{10.14}$$

The last sum is the sum over all states, s, for a particle in a box. We recognize this as the one-particle partition function, Z_1, for the translational motion of one particle in a box:

$$\bar{N} = e^{\mu/kT} Z_1 \, , \tag{10.15}$$

and the chemical potential therefore is:

$$\mu = kT \ln(\bar{N}/Z_1) \, . \tag{10.16}$$

For an ideal gas - that is for a particle in a box - we found that the one-particle partition function is

$$Z_1 = n_Q V \, , \tag{10.17}$$

where

$$n_Q = \left(\frac{mkT}{2\pi h^2} \right)^{3/2} \, , \tag{10.18}$$

was called the quantum concentration. The chemical potential is therefore

$$\mu = kT \ln(\bar{N}/(n_Q V)) = kT \ln(\bar{n})/n_Q) \, , \tag{10.19}$$

where $\bar{n} = \bar{N}/V$.

10.2 Fermi gases

We can use a similar approach to determine the number of particles in a Fermi gas: We find the average number of particles in each state for a particle in a box, and then find the total average number of particles as the sum of the average number of particles in each state:

$$\bar{N} = \sum_s f(\varepsilon_s; \mu, T) \,, \tag{10.20}$$

where the sum is over all the states for a single particle in a box.

However, we are usually instead interested in understanding the behavior in a system with a given number, N, of particles and not a given chemical potential. How can we transform the results we have for a given chemical potential to a system with a given number of particles? Since we know how to calculate the (average) number of particles, $\bar{N}$, in a system, we can simply find the chemical potential, $\mu(V, T, N)$, for which the average number of particles, $\bar{N}$, is equal to the number of particles, N: $\bar{N} = N$. From a more practical point of view, this means that we first calculate $\bar{N} = \bar{N}(T, V, \mu)$ for a given μ, and then find μ from the equation

$$N = \bar{N} = \bar{N}(T, V, \mu) \,. \tag{10.21}$$

10.2.1 Zero temperature limit

Let as start at the simplest case. At very low temperatures, where $T = 0$, the Fermi distribution is a step function. This means that all the states below the chemical potential at $T = 0$ – the Fermi energy – are occupied by one particle, and none of the states above the chemical potential are occupied. (We recall that the chemical potential at $T = 0$ is called the Fermi energy, $\varepsilon_F = \mu(T = 0)$.)

In this case, it is simple to find the number of particles in the system. Since all the states below ε_F have one particle in them, we simply need to count the number of states with energies below ε_F and this will be the (average) number of particles in the gas.

In general, we find the average number of particles in the gas from

$$\bar{N} = \sum_s \bar{N}_s = \sum_s f(\varepsilon_s; \mu, T) \,, \tag{10.22}$$

where the sum is over all the states s of the system. The states of a particle in a box are given as (n_x, n_y, n_z, σ). We can sketch the states in the n_x, n_y, n_z space as illustrated in fig. 10.3. We see that for each set of integers n_x, n_y, n_z we have two states. If we look at a "volume" $\Delta V = \Delta n_x \Delta n_y \Delta n_z$ in this space, we know that $\Delta n_x = \Delta n_y = \Delta n_z = 1$ we will have 2 states in this volume (as long as the volume is in octant where n_x, n_y, and n_z all are positive). We can therefore introduce a **density of states** in the n_x, n_y, n_z-space: $D(n_x, n_y, n_z)$ so that the number of states, $\Delta \mathcal{N}$, in the volume from n_x, n_y, n_z to $n_x + \Delta n_x, n_y + \Delta n_y, n_z + \Delta n_z$ is

$$\Delta \mathcal{N} = D(n_x, n_y, n_z)\Delta n_x \Delta n_y \Delta n_z \ . \qquad (10.23)$$

The density of states for this problem – a particle in a box – is uniform in n_x, n_y, n_z-space:

$$D(n_x, n_y, n_z) = \begin{cases} 2 & \text{when } n_x > 0, n_y > 0, n_z > 0 \\ 0 & \text{otherwise} \end{cases} \ . \qquad (10.24)$$

The number of states in a volume V is therefore simply $D(n_x, n_y, n_z)V = 2V$ in n_x, n_y, n_z-space.
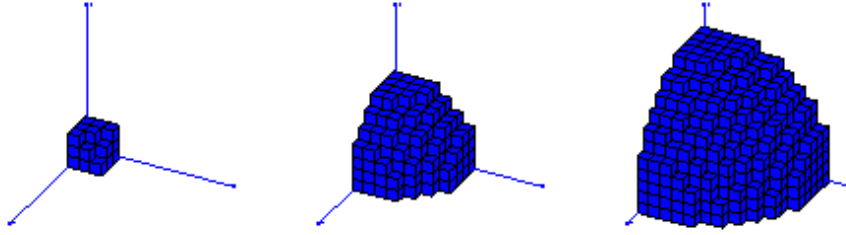

Fig. 10.3 Illustration of the states of a particle in a box. Each vertice of a voxel represents a single state. The three figures illustrates the states that are below n_F for $n_F = 3, 7, 11$.

For $T = 0$ we wanted to count all states with energies below ε_F. The energy of a state is

$$\varepsilon(n_x, n_y, n_z) = a\left(n_x^2 + n_y^2 + n_z^2\right) = an^2 \ , \qquad (10.25)$$

which means that the energy only depends on the distance n from the origin in n_x, n_y, n_z-space. The condition that $\varepsilon \leq \varepsilon_F$ therefore corresponds to

$$\begin{aligned} \varepsilon &\leq \varepsilon_F \\ an^2 &\leq \varepsilon_F \\ n &\leq \sqrt{\frac{\varepsilon_F}{a}} = n_F \ . \end{aligned} \qquad (10.26)$$

To find the number of states with $\varepsilon \leq \varepsilon_F$ we must therefore count the number of states in the n_x, n_y, n_z-space with $n \leq n_F$, that is, we must count all the states inside a sphere with radius n_F.

Let us follow two approaches to find the number of states in this volume. First, we simply use that the denstiy of states in n_x, n_y, n_z-space is uniform, and that the number of states therefore is the volume of the sphere with radius n_F multiplied with the density of states which is 2, taking into account that only positive values of n_x, n_y, n_z. Using this argument, the number of states inside n_F is

$$\bar{N} = 2 \cdot V_F = \underbrace{2}_{\text{2 spins}} \cdot \underbrace{\frac{1}{8}}_{n_x,n_y,n_z>0} \cdot \underbrace{\frac{4\pi}{3}n_F^3}_{\text{volume of sphere}} = \frac{\pi}{3}n_F^3 \ . \tag{10.27}$$

However, it is instructive to calculate $\bar{N}$ following a more formal approach, since this approach can be generalized to the case where $T > 0$. The total average number of particles in the system is the sum of the average number of particles in each state:

$$\bar{N} = \sum_s \bar{N}_s = \sum_s f(\varepsilon_s; \mu, T) \ , \tag{10.28}$$

where the states now are given as (n_x, n_y, n_z, σ):

$$\bar{N} = \sum_{n_x} \sum_{n_y} \sum_{n_z} \sum_{\sigma} f(\varepsilon(n_x, n_y, n_z); \mu, T) \ . \tag{10.29}$$

If we assume that the sum will be over many states, we can approximate this sum by an integral over (n_x, n_y, n_z), where we also must include the density of states:

$$\bar{N} = \iiint f(\varepsilon(n_x, n_y, n_z); \mu, T) D(n_x, n_y, n_z) dn_x dn_y dn_z \ . \tag{10.30}$$

For $T = 0$, $f(\varepsilon)$ becomes a step function, and we only need to include the n_x, n_y, n_z values that satisfy $n \leq n_F$:

$$\bar{N} = \iiint_{n \leq n_F} D(n_x, n_y, n_z) dn_x dn_y dn_z \ . \tag{10.31}$$

Now, we can use our knowledge from calculus to spherical coordinates in the n_x, n_y, n_z space. The integral transformation needed to go from Cartesian to spherical coordinates is to replace $dn_x dn_y dn_z = 4\pi n^2 dn$. However, when we integral in spherical coordinates, we must remember that we only include $1/8$ of the sphere since we only allow positive coordinates. The integral transform is therefore

$$\bar{N} = \iiint_{n \leq n_F} D(n_x, n_y, n_z) dn_x dn_y dn_z = \int_0^{n_F} D(n_x, n_y, n_z) \frac{4\pi}{8} n^2 dn \ . \tag{10.32}$$

We insert $D(n_x, n_y, n_z) = 2$, getting:

$$\bar{N} = \int_0^{n_F} 2\frac{4\pi}{8} n^2 dn = \int_0^{n_F} \pi n^2 dn = \ . \tag{10.33}$$

From this equation, we see that we can interpret πn^2 as the density of states in n-space (which here is different from n_x, n_y, n_z-space): $D(n) = \pi n^2$.

This integral can be easily solved:

$$\bar{N} = \int_0^{n_F} \pi n^2 dn = \frac{\pi n_F^3}{3} \ . \tag{10.34}$$

This is, of course, the same as we found in eq. 10.35.

Solving for the chemical potential. We insert $n_F = \sqrt{\varepsilon_F/a}$ to find the average number of particles in terms of the chemical potential at $T = 0$:

$$\bar{N} = \frac{\pi}{3}n_F^3 = \frac{\pi}{3}\frac{\varepsilon_F^{3/2}}{a^{3/2}} \ . \tag{10.35}$$

We can solve for ε_F, getting:

$$\left(\frac{3\bar{N}}{\pi}\right)a^{3/2} = \varepsilon_F^{3/2} \ , \tag{10.36}$$

and therefore

$$\left(\frac{3\bar{N}}{\pi}\right)^{2/3}a = \varepsilon_F \ . \tag{10.37}$$

We recall that a also includes the volume V of the system:

$$a = \frac{h^2}{8mV^{2/3}} \ , \tag{10.38}$$

which gives

$$\varepsilon_F = \left(\frac{3\bar{N}}{\pi}\right)^{2/3}\frac{h^2}{8mV^{2/3}} = \frac{h^2}{8m}\left(\frac{3}{\pi}\right)^{2/3}\left(\frac{\bar{N}}{V}\right)^{2/3} \ . \tag{10.39}$$

We repeat the argument that lead to this conclusion: At $T = 0$ all the states up to the chemical potential are occupied by one particle. We can therefore find the average number of particles, $\bar{N}$, in the gas when the chemical potential is given, by summing up how many staes we have below the chemical potential. We reverse this argument, and find the chemical potential given the number of particles, which gives us $\mu(T = 0) = \varepsilon_F$ as a function of $\bar{N}$ (and V) - which is what we found above.

Average energy at $T = 0$. We can also find the average energy of the gas at $T = 0$ using a similar approach. The average energy of a state (n_x, n_y, n_z, σ) is $N(n_x, n_y, n_z, \sigma) \cdot \varepsilon(n_x, n_y, n_z, \sigma)$. We can therefore find the total average energy by summing the average energies for all the states:

$$\bar{E} = \sum_{(n_x, n_y, n_z, \sigma)} N(n_x, n_y, n_z, \sigma) \cdot \varepsilon(n_x, n_y, n_z, \sigma) \ . \tag{10.40}$$

The energy only depends on the magnitude of (n_x, n_y, n_z), $\varepsilon = an^2$, we can therefore replace the sum with an integral over n:

$$\bar{E} = \int_0^\infty an^2 f(\varepsilon; \mu, T)D(n)dn \ , \tag{10.41}$$

where $D(n)$ is the density of states in the n-space and $D(n)dn$ gives the number of states in the interval from n to $n + dn$.

How can we solve this integral? We will work more with this in general in the following, but for the $T = 0$ case, the integral reduces to a simple form because $f(\varepsilon; \mu, T = 0) = 0$ when $n > n_F$ and 1 otherwise. The integral therefore becomes:

$$\bar{E} = \int_0^{n_F} an^2 D(n)dn , \qquad (10.42)$$

where $D(n)dn = \pi n^2 dn$:

$$
\begin{aligned}
\bar{E} &= \int_0^{n_F} an^2 \pi n^2 dn \\
&= \pi a \int_0^{n_F} n^4 dn \\
&= \frac{\pi}{5} an_F^5 \\
&= \underbrace{(an_F^2)}_{=\varepsilon_F} \cdot \underbrace{\left(\frac{\pi}{3} n_F^3\right)}_{\bar{N}} \cdot \frac{2}{5} \\
&= \frac{2}{5} \bar{N} \varepsilon_F .
\end{aligned}
\qquad (10.43)
$$

(Notice that we used the result $\bar{N} = (\pi/3)n_F^3$ from eq. 10.35). This result is surprisingly simple! This simplicity is not that surprising: Since we are at $T = 0$ we have filled up all the states up to the level ε_F, starting from the states with lowest energy. Because of the Pauli principle we can only have one Fermion in each state, and the particles will therefore be distributed across a range of states with a range of energies. You can gain some inituition about these states from the illustration of the states in n_x, n_y, n_z-space in fig. 10.3. However, since the energies of the states increases rapidly with distance from the origin, $\varepsilon = an^2$, most of the energy comes from the states far from the origin. The result is that $\bar{E} = (2/5)N\varepsilon_F$, which means that many of the states are near ε_F. We will gain more intuition into this in the next section.

The result we have found also give us useful physical insights into the quantuum effects on the behavior of a quantum gas. We see that if we keep N constant for the gas, but compress the system (decrease V), then ε_F will increase (from eq. 10.39 we know that $\varepsilon_F \propto (\bar{N}/V)$), and therefore the energy will increase. This effect gives rise the a repulsion due to Fermi-exclusion.

10.2.2 Density of states

We introduced the density of states in both n_x, n_y, n_z-space and in n-space in order to describe the number of states in a small interval around a point (n_x, n_y, n_z) or n.

The density of states in n_x, n_y, n_z-space was $D(n_x, n_y, n_z)$. By this we meant that the number of states between (n_x, n_y, n_z) and $(n_x + dn_x, n_y + dn_y, n_z + dn_z)$ is

$$\mathcal{N} = D(n_x, n_y, n_z) dn_x dn_y dn_z \; , \tag{10.44}$$

where we found that $D(n_x, n_y, n_z) = 2$ when n_x, n_y, and n_z all are positive, and zero otherwise.

We have similarly introduced a density of states in n-space - so that the number of states with magnitude n between n and $n + dn$ is

$$D(n) dn = 2 \cdot \frac{1}{8} \cdot 4\pi n^2 dn = \pi n^2 dn \; , \tag{10.45}$$

where the factor 2 again comes from the two spin states per **n** value and the factor of $1/8$ is included because only positive values of n_x, n_y, and n_z are used, hence only $1/8$ of the volume of a sphere with radius n is in the first octant. We therefore call $D(n) = \pi n^2$ the density of states for the three-dimensional ideal gas. Notice that the density of states would be different for a one- or a two-dimensional gas - the n-dependence would be different!

However, the density of states in n-space is not that useful since the occupation number - $f(\varepsilon, \mu, T)$ - is given in terms of ε. If we want to calculate average values - such as the average number of particles or the average energy - we perform the "sums" over (n_x, n_y, n_z) which we convert to integrals of n (since all quantities only depend on the length of (n_x, n_y, n_z) - and since the number of states is large so that the integral is a good approximation for the sum):

$$\bar{N} = \sum_{(n_x, n_y, n_z)} 2 f(\varepsilon(n_x, n_y, n_z); \mu, T) = \int_0^\infty f(\varepsilon(n), \mu, T) D(n) dn \; . \tag{10.46}$$

Similarly, we find the average energy from a similar integral:

$$\bar{U} = \sum_{(n_x, n_y, n_z)} 2\varepsilon(n_x, n_y, n_z) f(\varepsilon(n_x, n_y, n_z); \mu, T) = \int_0^\infty \varepsilon(n) f(\varepsilon(n); \mu, T) D(n) dn \; , \tag{10.47}$$

Now - we can evaluate this integral by inserting $\varepsilon(n) = an^2$. Or we can change integration variable in the integral, and instead integrate over ε. That is, we introduce the variable $\varepsilon(n)$ and the differential:

$$d\varepsilon(n) = \frac{d\varepsilon}{dn} dn \; , \tag{10.48}$$

giving the integrals:

$$\bar{N} = \int_0^\infty f(\varepsilon; \mu, T) D(n(\varepsilon)) \frac{1}{d\varepsilon/dn} d\varepsilon \; , \tag{10.49}$$

and

$$\bar{U} = \int_0^\infty \varepsilon f(\varepsilon; \mu, T) D(n(\varepsilon)) \frac{1}{d\varepsilon/dn} d\varepsilon \ . \qquad (10.50)$$

From these expressions we see that we can interpret

$$D(n(\varepsilon)) \frac{1}{d\varepsilon/dn} d\varepsilon = D(\varepsilon) d\varepsilon \ , \qquad (10.51)$$

as the density of states in ε space. The quantity $D(\varepsilon)d\varepsilon$ gives the number of states with energies between ε and $\varepsilon + d\varepsilon$.

Let us find the density of states in energy space for the three-dimensional gas. We find it using the integral transformation we introduced above:

$$D(n)dn = D(\varepsilon)d\varepsilon \ , \qquad (10.52)$$

and therefore

$$D(n(\varepsilon)) \frac{1}{d\varepsilon/dn} = D(\varepsilon) \ , \qquad (10.53)$$

where we now use that

$$\varepsilon(n) = \frac{\hbar}{2m} \left(\frac{\pi}{L}\right)^2 n^2 = an^2 \ , \qquad (10.54)$$

and therefore we find:

$$n = (\varepsilon/a)^{1/2} \ , \qquad (10.55)$$

and that

$$\frac{d\varepsilon}{dn} = 2an \ , \qquad (10.56)$$

which we insert in eq. 10.53 to get

$$\begin{aligned}
D(\varepsilon) &= D(n) \frac{1}{d\varepsilon/dn} \\
&= \pi n^2 \frac{1}{2an} \\
&= \frac{\pi}{2a} n \\
&= \frac{\pi}{2a} \sqrt{\frac{\varepsilon}{a}} \\
&= \frac{\pi}{2a^{3/2}} \varepsilon^{1/2} \\
&= \frac{\pi(8m)^{3/2}}{2h^3} V \sqrt{\varepsilon} \\
&= \frac{3N}{2\varepsilon_F^{3/2}} \sqrt{\varepsilon} \ .
\end{aligned} \qquad (10.57)$$

The nice thing about this expression is that it can be interpreted in the same plot - in the same space as we say here - as the distribution function f. This is illustrated in fig. 10.4, where we have plotted both the density of states $D(\varepsilon)$, $f(\varepsilon;\mu,T)$ and their product in the same plot.
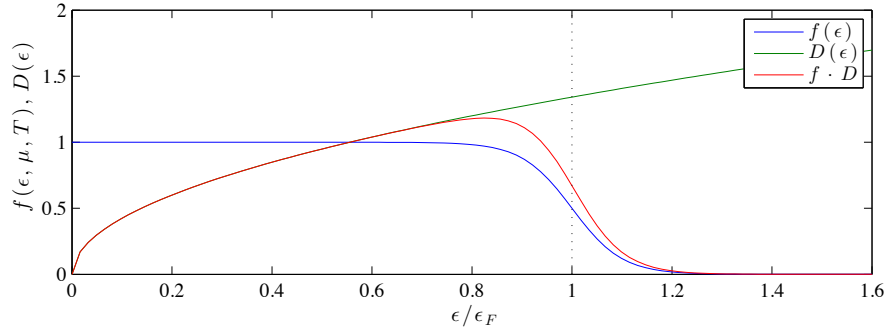

Fig. 10.4 Plot of the density of states, $D(\varepsilon)$, the number of particles in a state with energy ε, $f(\varepsilon;\mu,T)$, and their product for $kT = 0.25\cdot\varepsilon_F$.

10.2.3 Behavior at $T = 0$

We can use fig. 10.4 to gain more insight into the system at $T = 0$. In this case, the distribution function $f(\varepsilon;\mu,T)$ is a step function with the step at ε_F. We can therefore think of what happens at $T = 0$ in a slightly different way: We can assume that we have a given number of particles N. These particles will fill up all the states, starting with the states with the lowest energy first. Since two particles cannot occupy the same state, we fill in the density of states, $D(\varepsilon)$, function starting from $\varepsilon = 0$ and then up to ε_F, as illustrated in fig. 10.5. In this case, it is simple to find the average number of particles – it is the area under the $D(\varepsilon)$ curve from 0 to ε_F:

$$
\begin{aligned}
\bar{N} &= \int_0^\infty f(\varepsilon;\mu,T)D(\varepsilon)d\varepsilon \\
&= \int_0^{\varepsilon_F} D(\varepsilon)d\varepsilon \\
&= \int_0^{\varepsilon_F} \frac{\pi}{2a}\sqrt{\frac{\varepsilon}{a}}d\varepsilon \\
&= \frac{\pi}{2a}\frac{1}{\sqrt{a}}\frac{2}{3}\varepsilon_F^{3/2} ,
\end{aligned}
\tag{10.58}
$$

where we have inserted $D(\varepsilon) = (\pi/2a)\sqrt{\varepsilon/a}$. This result corresponds to what we found previously. However, it is simple to see from the $\varepsilon^{1/2}$ dependence of $D(\varepsilon)$ that the average number of particles will depend on $\varepsilon_F^{3/2}$.
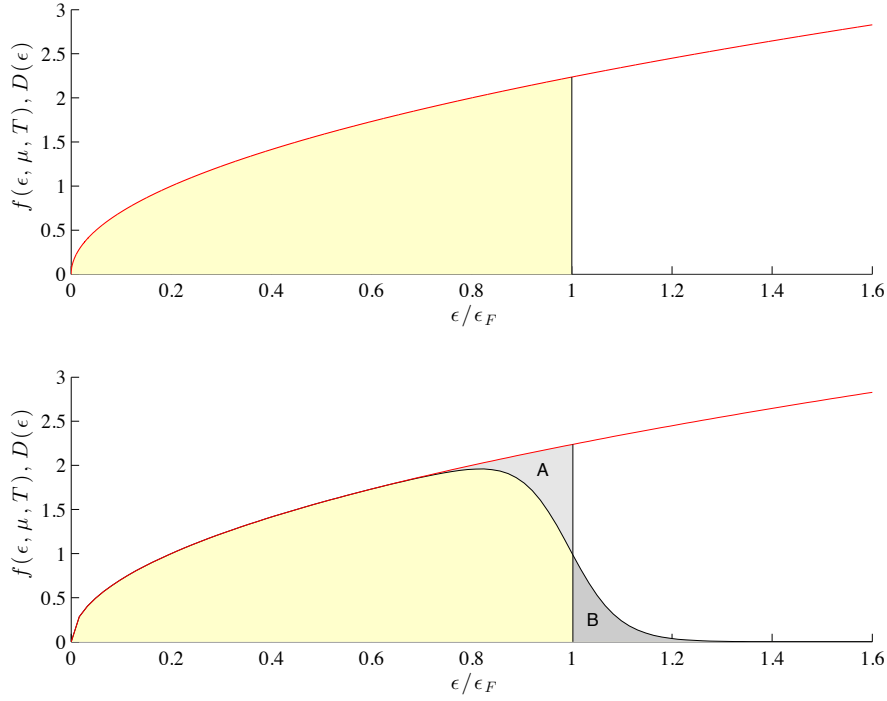

Fig. 10.5 (Top) At $T = 0$ all the states up to ε_F are filled. (Bottom) For $T > 0$ the particles in the states in area A have been moved into the the states B with higher energies for $kT = 0.25\varepsilon_F$.

10.2.4 Qualitative behavior at low temperatures

We have found the chemical potential, ε_F, at $T = 0$. How does the chemical potential depend on temperature at low temperatures? We can gain insights just from the behavior of $D(\varepsilon)$ itself. If we look at a gas with a given number N of particles (such as a given number of free electrons in an electron gas), then we can solve the equation

$$N = \bar{N} = \int_0^\infty f(\varepsilon; \mu(T), T) D(\varepsilon) d\varepsilon , \qquad (10.59)$$

for $\mu(T)$. What does this integral represent? It represents the area under the curve $f(\varepsilon; \mu, T) \cdot D(\varepsilon)$ as illustrated in fig. 10.5. Since the area corresponds to the number

of particles, and we assume that the number of particles is conserved, the area must be conserved when the temperature is increased from $T = 0$.

What happens as T is increased? Some of the particles in the states below the chemical potential (area A) are moved into states above the chemical potential (area B) as illustrated in fig. 10.5. However, the number of particles removed from states below the chemical potential (area A), must be equal to the number of particles added to states above the chemical potential (area B) in order for the number of particles to remain constant.

Now, if we assume that the chemical potential μ does not change when T is increased, we see that area B will be larger than area A because $D(\varepsilon)$ is an increasing function and $f(\varepsilon; \mu, T)$ is symmetric around $\varepsilon = \mu$. This is illustrated in the magnification shown in fig. 10.6. The top figure shows what happens if we assume that the chemical potentia $\mu(T) = \varepsilon_F$ also when $T > 0$. In this case the area B is larger than the area A. This is not that easy to see from the figures, since the differences are rather small.

How should $\mu(T)$ depend on T in order to increase the area A and decrease the area B? To get this argument right, it is important to realize what areas we really are to compare. We have illustrated this in the bottom figure in fig. 10.6. Here we have illustrated the chemical potential by the dotted line. The chemical potential is smaller than ε_F in this figure. We have also illustrated the relevant areas: It is the area below ε_F and above ε_F we should compare. (Not the area below and above μ – can you see the difference?). At $T = 0$ the area below $D(\varepsilon)$ corresponds to the number of particles in the system.

In the top figure in fig. 10.6 we have argued that area B is slightly larger than area A. In the bottom figure in fig. 10.6 we see that area A is clearly larger than area B. This means that the correct value for μ lies somewhere between $\mu = \varepsilon_F$ in the top figure and $\mu = 0.99 \cdot \varepsilon_F$ in the bottom figure. This means that μ must be smaller than ε_F, but not as small as illustrated in this figure.

Conclusion: $\mu(T)$ must be a decreasing function of T near $T = 0$.

10.2.5 Quantitative description of low temperature behavior

We can also devise a simplified quantitative argument to estimate how the energy $\bar{E}$ depends on the temperature and then use this argument to find how μ depends on T near $T = 0$. The average energy of the system is

$$\bar{E} = \int_0^\infty \varepsilon f(\varepsilon; \mu, T) D(\varepsilon) d\varepsilon \ . \tag{10.60}$$

Let us now assume that the number of particles, N, is given so that $\mu = \mu(T)$. We can then find the heat capacity (at constant volume, since we still work in a T, V system) from
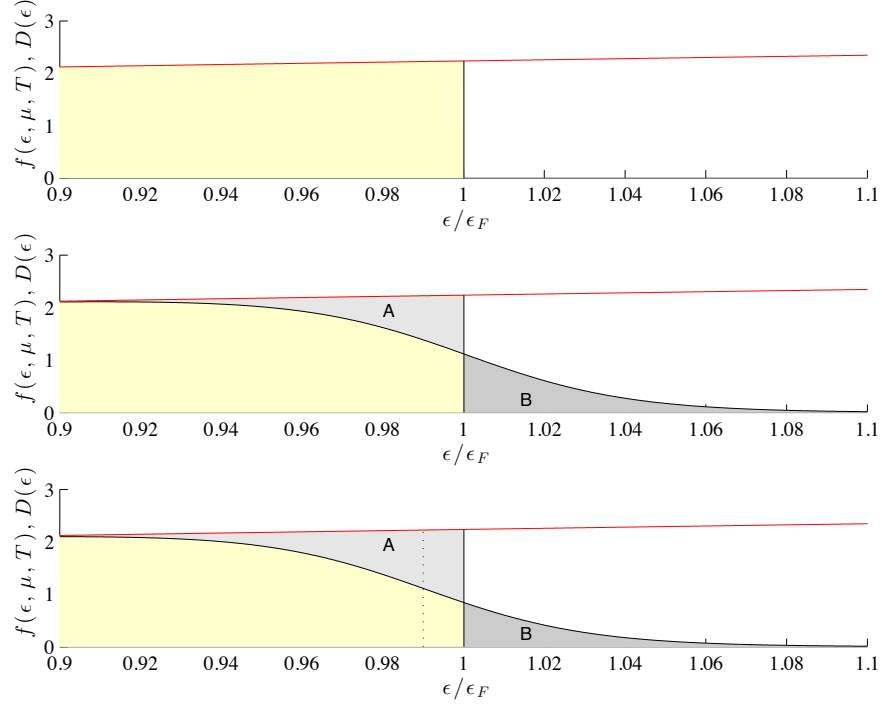
Fig. 10.6 Plot of $f(\varepsilon;\mu,T=0)\cdot D(\varepsilon)$ (top), $f(\varepsilon;\varepsilon_F,T=0.1T_F)\cdot D(\varepsilon)$ (middle), and $f(\varepsilon;\mu,T=0.1T_F)\cdot D(\varepsilon)$ (bottom) where $T_F=\varepsilon_F/k$.

$$C_V = \left(\frac{d\bar{E}}{dT}\right) = \int_0^\infty \varepsilon D(\varepsilon)\frac{d}{dT}f(\varepsilon;\mu(T),T)d\varepsilon \ , \qquad (10.61)$$

where there are two T-dependencies in f – both a direct dependency and an indirect dependency through $\mu(T)$:

$$\frac{df(\varepsilon;\mu(T),T)}{dT} = \frac{\partial f}{\partial T} + \frac{\partial f}{\partial \mu}\frac{d\mu}{dT} \ . \qquad (10.62)$$

This gives

$$C_V = \int_0^\infty \varepsilon \frac{\partial f}{\partial T}D(\varepsilon)d\varepsilon + \frac{d\mu}{dT}\int_0^\infty \varepsilon \frac{\partial f}{\partial \mu}D(\varepsilon)d\varepsilon \ . \qquad (10.63)$$

We can do the same for $\bar{N}$:

$$\bar{N} = \int_0^\infty f(\varepsilon;\mu(T),T)D(\varepsilon)d\varepsilon \ , \qquad (10.64)$$

$$\frac{d\bar{N}}{dT} = \int_0^\infty \frac{\partial f}{\partial T}D(\varepsilon)d\varepsilon \ , \qquad (10.65)$$

$$0 = \int_0^\infty \frac{\partial f}{\partial T} D(\varepsilon) d\varepsilon + \frac{d\mu}{dT} \int_0^\infty \frac{\partial f}{\partial \mu} D(\varepsilon) d\varepsilon \ . \tag{10.66}$$

(Where we have used that $(d\bar{N}/dT)$ is constant, since the number of particles in the system does not change when we change the temperature if the number of particles is constant). Up to now we have not done any approximations. Now, we see that f is a rapidly varying function of ε around μ:

$$\frac{\partial f}{\partial \mu} = \frac{e^{(\varepsilon - \mu)/kT}}{\left(e^{(\varepsilon - \mu)/kT} + 1\right)^2} \ . \tag{10.67}$$

We can therefore approximate the second integral in eq. 10.63 by

$$\int_0^\infty \varepsilon D(\varepsilon) \frac{\partial f}{\partial \mu} d\varepsilon \simeq \mu \int_0^\infty D(\varepsilon) \frac{\partial f}{\partial \mu} d\varepsilon \ , \tag{10.68}$$

where the right hand side now corresponds to the second integral in eq. 10.66. We can therefore replace

$$\mu int_0^\infty \frac{\partial f}{\partial \mu} D(\varepsilon) d\varepsilon = -\frac{\mu}{d\mu/dT} \int_0^\infty \frac{\partial f}{\partial T} D(\varepsilon) d\varepsilon + \ . \tag{10.69}$$

We replace this into the equation for C_V in eq. 10.66 getting

$$C_V \simeq \int_0^\infty \varepsilon \frac{\partial f}{\partial T} D(\varepsilon) d\varepsilon - \mu \int_0^\infty \frac{\partial f}{\partial T} D(\varepsilon) d\varepsilon = \int_0^\infty (\varepsilon - \mu) \frac{\partial f}{\partial T} D(\varepsilon) d\varepsilon \ . \tag{10.70}$$

We will use the same approximation once more, but this time argue that $\partial f/\partial T$ falls off rapidly with ε away from μ, but that $D(\varepsilon)$ varies slowly, so that we can assume that $D(\varepsilon)$ is approximately constant and equal to $D(\mu)$, simplifying the integral to:

$$C_V \simeq \int_0^\infty (\varepsilon - \mu) \frac{\partial f}{\partial T} D(\varepsilon) d\varepsilon \simeq D(\mu) \int_0^\infty (\varepsilon - \mu) \frac{\partial f}{\partial T} d\varepsilon \ . \tag{10.71}$$

Here, we need $\partial f/\partial T$:

$$\frac{\partial F}{\partial T} = \frac{(\varepsilon - \mu)}{kT^2} \frac{e^{(\varepsilon - \mu)/kT}}{\left(e^{(\varepsilon - \mu)/kT} + 1\right)^2} \ . \tag{10.72}$$

Now, we are near an integral we can solve. We introduce a new integration variable, $x = (\varepsilon - \mu)/kT$, so that $d\varepsilon = kT dx$, which gives:

$$C_V \simeq D(\mu) k^2 T \int_{-\mu/kT}^\infty \frac{x^2 e^x}{(e^x + 1)^2} dx \ , \tag{10.73}$$

where again the integral varies rapidly around $x = 0$, and the lower bound therefore can be set to be approximately $-\infty$, and we can solve the integral exactly:

$$C_V \simeq D(\mu)k^2T \int_0^\infty \frac{x^2 e^x}{(e^x+1)^2} dx = k^2 T D(\mu)\frac{1}{3}\pi^2 . \qquad (10.74)$$

We may also approximate $D(\mu) \simeq D(\varepsilon_F)$, which gives

$$D(\mu) \simeq D(\varepsilon_F) = \frac{3N}{2}\frac{1}{\varepsilon_F} = \frac{3}{2}\frac{1}{NkT_F} , \qquad (10.75)$$

and therefore

$$C_V \simeq \frac{1}{2}\pi^2 Nk \frac{T}{T_F} = aNT , \qquad (10.76)$$

where $kT_F = \varepsilon_F$, that is, $T_F = \varepsilon_F/k$, and a is a constant that does not depend on N or T. A typical values for T_F for an electron gas is $T_F \simeq 5 \cdot 10^4$K.

This long derivation shows that the heat capacity due to an electron gas (or another Fermi gas) is proportional to T at low temperatures (T small compared with T_F).

10.3 Photon Systems

Let us now use the theory we have developed to address the behavior of a photon gas - a system with electromagnetic waves inside a container – in equilbrium with the container walls. In this case the walls will absorb and emit electromagnetic wave (packets) - so the number of photons is not conserved.

For a container of length L, we assume that the field only consists of standing waves (in equilbrium). These waves can therefore have frequencies $f = c/\lambda$ and corresponding energies $\varepsilon = nhf = n\hbar\omega$, where n is an integer corresponding to the state.

(The integer n comes from the number of half-wavelengths that make up the length L: $L = (n/2)\lambda$, where n is an integer.)

This corresponds to the harmonic oscillator we have already studied.

We will now study the occupancy probability for these states. We can assume that the system has constant volume V and temperature T, and that since photons are continually created and destroyed - the chemical potential for the system is therefore zero.

We can then use the Bose-Einstein distribution law:

$$f_{BE}(\varepsilon, \mu, T) = \frac{1}{e^{(\varepsilon-\mu)/kT} - 1} , \qquad (10.77)$$

which we can simplify since $\mu = 0$ to

$$f_{BE}(\varepsilon, \mu = 0, T) = \frac{1}{e^{(\varepsilon/kT} - 1} , \qquad (10.78)$$

which is the same as we found for the harmonic oscillator in the canonical ensemble.

This tells us the occupancy of a given energy level ε_s. In addition we need to know the density of states for the photon gas.

For particles (fotons) in a box, the possible (standing wave) solutions are

$$\lambda = \frac{2L}{n} , \frac{hn}{2L} , \tag{10.79}$$

where n is a positive integer. The energy of the photon is

$$\varepsilon = pc = \hbar\omega = \frac{hcn}{2L} , \tag{10.80}$$

instead of $\varepsilon = p^2/2m$ for classical particles.

This means that the energy of a photon generally is proportional to n while the energy of a classical moving particles (in an ideal gas / Fermi gas) is proportional to n^2.

This is also true in three dimensions, where the momentum is independent in the three direction, and equal to $hc\,n/2L$ in each direction:

$$\mathbf{p} = \frac{hc}{2L}(n_x, n_y, n_z) , \tag{10.81}$$

and the energy still is $\varepsilon = pc$, where p is the magnitude of $\mathbf{p}$:

$$\varepsilon = \frac{hc}{2L}\left(n_x^2 + n_y^2 + n_z^2\right)^{1/2} = \frac{hcn}{2L} . \tag{10.82}$$

In order to use the distribution function, we need to sum over all possible states (and their corresponding energies) to find the number of photons and the total energy of the photon gas.

Let us first look at the total energy - which we find by summing over all possible n-values - including the effect of two possible polarizations:

$$U = 2\sum_{n_x}\sum_{n_y}\sum_{n_z} \varepsilon(n_x, n_y, n_z) f_{BE}(\varepsilon, \mu = 0, T) , \tag{10.83}$$

where $\varepsilon = hcn/L$. Instead of summing, we integrate over n in n-space:

$$U = 2\int_0^\infty \frac{4\pi n^2}{8} \frac{hcn}{L} \frac{1}{e^{hcn/2LkT} - 1} \, dn . \tag{10.84}$$

We can now transform to a variable that simplifies the exponent, choosing $x = hcn/2LkT$, which gives $n = 2LkTx/hc$ and $dn = 2LkT/hc\,dx$:

$$U = \frac{8\pi(kT)^4 L^3}{(hc)^3} \int_0^\infty \frac{x^3}{e^x - 1} \, dx , \tag{10.85}$$

where the integral is $\pi^4/15$. Energy per volume is therefore then

$$\frac{U}{V} = \frac{8\pi^5}{15h^3c^3}(kT)^4 \,. \tag{10.86}$$

This is called the **Stehan-Boltzmann** law of radiation.

We can also find the frequency (or energy, since they are propotional $\varepsilon = h\nu$) distribution of the photon gas / blackbody radiation.

What does that mean? We can find for example how many photons are in the range from ν to $\nu + d\nu$, how many photons are in the range from ε to $\varepsilon + d\varepsilon$ - or preferrably – how much energy is in the corresponding range of frequencies / energies: We find this as the number of photons in the range multiplied by the energy per photon, ε.

We can read this directly from the integral, realizing that the integral for the total energy can be written as

$$U = \int_0^\infty \varepsilon_n D(n)dn = \int_0^\infty \varepsilon D(\varepsilon)d\varepsilon \,, \tag{10.87}$$

or if we are interested in the energy density (U/V) instead:

$$\frac{U}{V} = \int_0^\infty \frac{\varepsilon_n}{V}D(n)dn = \int_0^\infty \frac{\varepsilon}{V}D(\varepsilon)d\varepsilon \,, \tag{10.88}$$

which is what we just found above.

Starting from

$$U = 2\int_0^\infty \frac{4\pi n^2}{8}\frac{hcn}{L}\frac{1}{e^{hcn/2LkT}-1}dn \,. \tag{10.89}$$

we can instead insert $\varepsilon = hcn/2L$, getting

$$\frac{U}{V} = \int_0^\infty \frac{8\pi\varepsilon}{(hc)^3 e^{\varepsilon/kT}-1}d\varepsilon \,, \tag{10.90}$$

and we see that the energy density in the range ε to $\varepsilon + d\varepsilon$ is

$$u(\varepsilon) = \frac{8\pi}{(hc)^3}\frac{\varepsilon^3}{e^{\varepsilon/kT}-1} \,. \tag{10.91}$$

We can express it instead using ν where $\varepsilon = h\nu$:

$$u(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1}d\nu \,. \tag{10.92}$$

This is called the **Planck radiation law**.

We can plot this distribution in dimensionless form by plotting $x^3/(e^x-1)$ as a function of $x = \varepsilon/kT$.

This function has a maximum at $x = 2.82$, which corresponds to $\varepsilon = 2.82\,kT$.

This shows that the maximum energy (or frequency) increases with temperature. This law is called **Wien's law**. (Wien's displacement law).

This law implies that the temperature can been seen from the most prominent color - since the frequency of this this color is proportional to the temperature. (If we can consider the body we examine as blackbody radiation).

10.3.1 Entropy of the photon gas

We can find the entropy, since for constant volume we have

$$T dS = dU \, , \, dS = \frac{dU}{T} = \frac{4aT^3}{T} \, , \tag{10.93}$$

which we integrate from 0 to T, getting:

$$S(T) = 4a\frac{1}{3}T^3 = \frac{32\pi^5}{45}V\left(\frac{kT}{hc}\right)^3 k \, . \tag{10.94}$$

(We can find the total number of photon using the same formula, but with a different prefactor).

10.3.2 Radiation from a black body

What if we have a photon gas and we study the radiation emitted from a small whole in the container.

We say that such a hole radiates as a black body.

The energy flux is the rate of energy emission per unit area.

How much radiates out in a time dt?

The energy in the volume dV which is cdt times the opening area A times some geometric factor g (which is $1/4$ - see textbook and problems).

The flux is therefore

$$J = \frac{dE}{Adt} = \frac{udV}{Adt} = \frac{uAcdtg}{Adt} = ucg \, . \tag{10.95}$$

and

$$J = \frac{cU}{4V} = \frac{2\pi^5}{15}\frac{(kT)^4}{(hc)^3} = \sigma T^4 \, , \tag{10.96}$$

where σ is called the **Stefan-Boltmann** constant.

And the law is called **Stefan's law**.

This is from a black body - non-reflecting! - body with surface temperature T.

Applications: Cosmic black body background radiation, Emission and absorption (Kirchoffs law).

10.4 Phonon Systems

We have previously introduced the Einstein model - or the ideal crystal - as our model for a crystal. But in this system there are no interactions between the atoms/-particles. Does this have any consequence?

For the Einstein crystal we found that the heat capacity was:

$$C_V = 3Nk \frac{\left(\frac{\varepsilon}{kT}\right)^2 e^{\varepsilon/kT}}{\left(e^{\varepsilon/kT} - 1\right)^2} \ . \tag{10.97}$$

where N now is the number of atoms/particles, so that $3N$ is the number of oscillators.

What happens when $\varepsilon \ll kT$ for this model? In that range the heat capacity approaches a constant: $3Nk$. This corresponds to the equipartition theorem.

What happens for small temperatures, when $\varepsilon \gg kT$? In this range the heat capacity goes to zero exponentially. This is not in correspondence with experiments, which show that the heat capacity goes to zero at T^3 in the low temperature limit.

What went wrong?

We have ignored interactions among the atoms - which probably may be important for lattice vibrations.

Mainly because there are different vibration modes in systems with many atoms - the atoms may vibrate together to form low frequency modes. At low temperatures the high frequencies (high energy) modes are frozen out, but then the low frequency (low energy) modes become more important. By only looking at single atoms we have overlooked collective modes that have lower energy. Therefore the heat capacity goes to zero slower than predicted by the Einstein model.

The vibration modes in a crystal resembles electromagnetic waves:

They are waves, but they have smaller velocities (much smaller of course). We will here assume that the speed is a constant c_s - even if it acutally depends on the wave length in a crystal.

They have three polarizations. The transverse and one longitudinal. The polarizations really have different velocities. At first we will ignore this effect.

The waves cannot have all possible wavelengths, because the atoms are on a lattice with a given lattice spacing, and we cannot resolve waves with wavelength shorter than (two times) the lattice spacing.

Let us assume that we can otherwise describe a phonon - a lattice vibration mode energy packet - just as we have described photons: with uniformly spaced energy levels:

$$\varepsilon_s = h\nu = \frac{hc_s}{\lambda} = \frac{hc_s n}{2L} \ , \tag{10.98}$$

where L is the system size. Again n is the magnitude of the **n** vector in n-space.

We also assume that phonons are bosons with $\mu = 0$, so that the distribution function is given by the Bose-Einstein distribution:

$$f_{BE} = \frac{1}{e^{\varepsilon/kT} - 1} \ . \tag{10.99}$$

We find the energy and the number of phonons by summing over all possible **n** values:

$$U = 3 \sum_{n_x} \sum_{n_y} \sum_{n_z} \varepsilon(\mathbf{n}) f(\varepsilon, \mu = 0, T) \ . \tag{10.100}$$

The main difference with the crystal lattice is that not all values are possible - we can only have some values for **n**.

Let us look at the x-direction.

Along this direction we have $N_x = (N)^{1/3}$ atoms as shown in the figure.

This puts at limit on the maximum upper number of n.

This should correspond to a cube in n-space.

The Debye approximation is to assume that we instead include all modes up to a radius n_D in n-space, but so that we ensure that the total number of modes is equal to $3N$:

$$3 \sum_{n_x} \sum_{n_y} \sum_{n_z} = \frac{3}{8} \int_0^{n_D} 4\pi n^2 dn = 3N \ , \tag{10.101}$$

This determines n_D. Since the integral is simply the volume of a sphere of radius n_D we find that

$$3N = \frac{3}{8} \frac{4\pi}{3} n_D^3 \ , \tag{10.102}$$

and therefore that

$$n_D = \left(\frac{6N}{\pi} \right)^{1/3} \ . \tag{10.103}$$

Now, we have a theory we can use to find the energy of the phonon gas using the approach we now are used to:

$$U = \sum_{n_x} \sum_{n_y} \sum_{n_z} \varepsilon_n f(\varepsilon_n, \mu = 0, T)$$

$$= \frac{3}{8} \int_0^{n_D} n^2 \frac{h\nu_n}{\exp(h\nu_n/kT) - 1} dn \ , \tag{10.104}$$

where

$$h\nu_n = \frac{hc_s n}{2L} \ . \tag{10.105}$$

The integral is therefore

$$U = \frac{3\pi}{2} \int_0^{n_D} \frac{hc_s}{2L} \frac{n^3}{\exp(hc_s n/2LkT) - 1} dn \ . \tag{10.106}$$

We introduce the new integration variable $x = hc_s n/2LkT$ getting:

$$x_D = \frac{hc_s n_D}{2LkT} = \frac{hc_s}{2kT} \left(\frac{6N}{\pi V} \right)^{1/3} = \frac{T_D}{T} \,, \tag{10.107}$$

where we call T_D the Debye temperature.

This gives - after some algebra:

$$U = \frac{9NkT^4}{T_D^3} \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx \,. \tag{10.108}$$

This integral cannot be solved analytically, but it is easy to solve numerically.

However, we can also find the high and low temperature limits directly by approximations.

In the high temperature limit the upper bound of the integral is much smaller than 1 and in this limit we can approximate $e^x = 1 + x$, and the integral becomes

$$\begin{aligned}
U &= \frac{9NkT^4}{T_D^3} \int_0^{T_D/T} \frac{x^3}{x} dx \\
&= \frac{9NkT^4}{T_D^3} \frac{1}{3} \left(\frac{T_D}{T} \right)^3 \\
&= 3NkT \,.
\end{aligned} \tag{10.109}$$

This corresponds to the equipartition principle.

In the lower limit, $T \ll T_D$, the upper limit is so large that we can replace it by infinity (since the e^x will go very quickly to zero, this is not a problem). The integral is therefore the same as we did for the photon gas - with value $\pi^4/15$, and the total energy is

$$U = \frac{3\pi^4}{5} \frac{NkT^4}{T_D^3} \,, \tag{10.110}$$

and the heat capacity in this limit is

$$C_V = \frac{12\pi^4}{5} \left(\frac{T}{T_D} \right)^3 Nk \,, \tag{10.111}$$

which agrees very well with experimental measurements.

We find the intermediate values by numerical integration.

For metals we need to include both the contribution from the phonos and the contributions from the electrons, so that the heat capacity has the behavior:

$$C_V = \gamma T + \frac{12\pi^4 Nk}{5T_D^3} T^3 \,, \tag{10.112}$$

when $T \ll T_D$ and $\gamma = \pi^2 Nk^2/2\varepsilon_F$.

If we now plot C_V/T as a function of T^2 we can check both constants in the resulting plot, which should be linear in T^2 with an intercept corresponding to γ.

What are typical values for T_D?

For lead 88K

For diamond 1860K

Above T_D you can get away with using the equipartition theorem since the heat capacity by then has reached 95% of its maximum value.

10.5 Boson Gas and Einstein Condensation

We have now looked at photons and phonons. For these particles we do not have a conservation law. What about other bosons, such as Helium-4? In this case the chemical potential is not zero - we will need to determine the chemical potential from the number of particles, just as we did for Fermions.

We start in the limit of small temperatures.

When $T = 0$ all the atoms will be in the lowest energy state.

For atoms in a box of volume $V = L^3$ the energy states are

$$\varepsilon = \frac{h^2}{8mL^2} \left(n_x^2 + n_y^2 + n_z^2 \right) , \tag{10.113}$$

so that the lowest energy state has energy

$$\varepsilon_0 = \frac{3h^2}{8mL^2} , \tag{10.114}$$

which is a very small value for realistic (macroscopic) values of L.

The Bose-Einstein distribution gives the average number of atoms in this state:

$$N_0 = \frac{1}{\exp((\varepsilon_0 - \mu)/kT) - 1} , \tag{10.115}$$

As the temperature approaches zero, we know that N_0 will be large, which means that $\exp((\varepsilon_0 - \mu)/kT) - 1$ must be close to 1. This means that the exponent is close to zero. In this limit, we can expand the exponent using $\exp(x) = 1 + x$, getting:

$$N_0 = \frac{1}{1 + (\varepsilon_0 - \mu)/kT - 1} = \frac{kT}{\varepsilon_0 - \mu} , \tag{10.116}$$

and therefore that $\mu = \varepsilon_0$ when $T = 0$ and then just a bit larger when T is small.

To make life simpler, let us change energy scales, so that $\varepsilon_0 = 0$. The result is then

$$N_0 = -\frac{kT}{\mu} , \ \mu = -\frac{kT}{N_0} . \tag{10.117}$$

10.5.1 Spacing of levels

What is really a realistic value for the spacing of energy levels?

The energy is

$$\varepsilon = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{10.118}$$

the energy difference between the lowest and the second lowest is therefore

$$\Delta\varepsilon = \frac{3h^2}{8mL^2} \tag{10.119}$$

Now if we look at Helium-4, $m = 6.6 \times 10^{-24}$g and $L = 1$cm, then

$$\frac{\Delta\varepsilon}{k} = 1.8 \times 10^{-14}\text{K}. \tag{10.120}$$

This is a small splitting!

How could this play an important physical role at temperatures which are Kelvin or at best a thousands of a Kelvin?

10.5.2 Approaching $T = 0$

What happens if we have a constant particle number, N, and we lower the temperature? Then the number of particles in the lowest leverl, N_0, approaches N - all the particles are in the state with the lowest energy.

This means that

$$N_0 = \frac{1}{\exp((\varepsilon_0 - \mu)/kT) - 1}, \tag{10.121}$$

approaches N (which is very large) when $\mu \simeq \varepsilon_0$.

For low temperatures we separate out the number of particles in the lowest state, and write

$$N = N_0 + \sum_{j=1}^{\infty} \frac{1}{\exp((\varepsilon_j - \mu)/kT) - 1}, \tag{10.122}$$

where we have removed the singularity in the lowest energy level.

We can change this to an integral (since the energy levels are very close), but then we need the density of states, $D(\varepsilon)$:

$$N = N_0 + \int_{\varepsilon_1}^{\infty} \frac{g(\varepsilon)}{\exp((\varepsilon - \mu)/kT) - 1} d\varepsilon, \tag{10.123}$$

Since ε_1 also is very small ($\varepsilon_1 \simeq 0$) and $g(0) = 0$, we can instead put 0 as the lower bound for the integral. In addition, we still assume that $\mu = 0$:

$$N = N_0 \int_0^\infty \frac{g(\varepsilon)d\varepsilon}{e^{\varepsilon/kT} - 1} \, , \tag{10.124}$$

where we now insert for $g(\varepsilon)$:

$$g(\varepsilon) = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2} V \sqrt{\varepsilon} \, , \tag{10.125}$$

and we introduce the variable $x = \varepsilon/kT$. The integral is then reduced to

$$N = N_0 + \frac{2}{\sqrt{\pi}} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \int_0^\infty \frac{x^{1/2}dx}{e^x - 1} \, , \tag{10.126}$$

where the integral is

$$\int_0^\infty \frac{x^{1/2}}{e^x - 1} dx = \frac{\sqrt{\pi}}{2} \cdot 2.612 = 2.315 \, , \tag{10.127}$$

and therefore we find

$$N = N_0 + 2.612 \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \, . \tag{10.128}$$

This expression is only valid for low temperatures, but the second term increases with temperature. What is the upper limit of validity of this expression? That is when N_0 is zero and all the particles are in higher energy levels, this occurs at a temperature T_C given by:

$$N = 2.612 \left(\frac{2\pi mkT_C}{h^2} \right)^{3/2} V \, , \tag{10.129}$$

which gives

$$kT_C = \frac{1}{\pi(2.612)^{2/3}} \frac{h^2}{2m} \left(\frac{N}{V} \right)^{2/3} \, . \tag{10.130}$$

The critical temperature T_C therefore depends both on details of the particles, through m, and on the density N/V of the system. (for low temperatures).

We can also use T_C to rewrite the expression for N:

$$N = N_0 + N \left(\frac{T}{T_C} \right)^{3/2} \, , \tag{10.131}$$

which gives

$$N_0 = N \left(1 - \left(\frac{T}{T_C} \right)^{3/2} \right) \, . \tag{10.132}$$

In the range $T < T_C$ we have Bose-Einstein condensation. At $T = 0$ all the particles are in the lowest energy state.

What happens when $T < T_C$? In this case our calculation is no longer valid. Instead we must include how the chemical potential varies with temperature. We can do this by solving the equation

$$N = \int_0^\infty \frac{g(\varepsilon)}{e^{(\varepsilon-\mu)/kT} - 1} d\varepsilon , \qquad (10.133)$$

numerically. We introduce new variables, $x = \varepsilon/kT_C$, $t = T/T_C$ and $c = \mu/kT_C$, and get the integral

$$2.315 = \int_0^\infty \frac{x^{1/2} dx}{e^{(x-c)/t} - 1} , \qquad (10.134)$$

which you now know how to solve.