

Fermi and Bose gases

Anders Malthe-Sørensen

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1 Thermodynamic identities and Legendre transforms

2 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.

We start from an individual particle.

For a single particle, we address its orbitals: Its possible quantum states, each of which corresponds to a solution of the Schrodinger equation for a single particle.

For many particles we will address how the “fill up” the various orbitals – where the underlying assumption is that we can treat a many-particle system as a system with the same energy levels as for a single particular system, that is as a system with no interactions between the states of the various particles. However, the number of particles that can occupy the same state 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.

We will now apply a Gibbs ensemble approach to study this system. This means that we will consider a system where μ, V, T is constant. We can use the Gibbs sum formalism to address the behavior of this system. We will consider a system that consists of a single orbital in equilibrium with a reservoir of constant chemical potential and constant temperature (and volume). From this we can find the average number of particles in a particular state, $\langle N \rangle_s$, and we will then sum the particles in all possible states to find the total number of particles.

This gives the number of particles as a function of the chemical potential. If, instead, we consider the number of particles as the given quantity, we can instead solve the equation for the number of particles to find the chemical potential. This is the general strategy of the approach we will take here.

We address a system consisting of a single orbital – a single state – with energy ϵ .

The Gibbs sum for this system is

$$Z_G = \sum_N \sum_s e^{-(\epsilon - N\mu)/kT} .$$

The probability to have N particles in a state of energy ϵ is then

$$P(\epsilon, N) = \frac{1}{Z_G} e^{-(\epsilon - N\mu)/kT} ,$$

and the average number of particles in this state is

$$\langle N \rangle(\epsilon, \mu, T) = \sum_N P(\epsilon, N) N ,$$

(The general strategy is then to solve this equation for $\mu(T, V, N)$).

Let us first address Fermions. In this case we can have $N = 0$ or $N = 1$ for a given state. The partition function is then

$$Z_G = e^{-(0-0\mu)/kT} + e^{-(\epsilon-1\mu)/kT} = 1 + e^{-(\epsilon-\mu)/kT} ,$$

and the average number of particles in this state is

$$\langle N \rangle = 0 \cdot 1 + 1 \cdot \frac{1}{Z_G} e^{-(\epsilon-\mu)/kT} = \frac{e^{-(\epsilon-\mu)/kT}}{e^{-(\epsilon-\mu)/kT} + 1} = \frac{1}{e^{(\epsilon-\mu)/kT} + 1} ,$$

we call this the Fermi-Dirac distribution and we often use the symbol $f(\epsilon, \mu, T)$ for the distribution function – corresponding to the average number of particles at the state with energy ϵ :

$$f(\epsilon, \mu, T) = \langle N \rangle(\epsilon, \mu, T) .$$

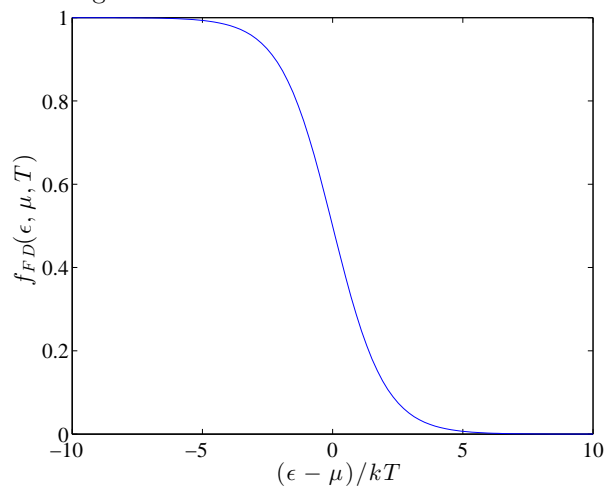
How does this function look? We can plot the function

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

as a function of x from $-\infty$ to $+\infty$ using the following script:

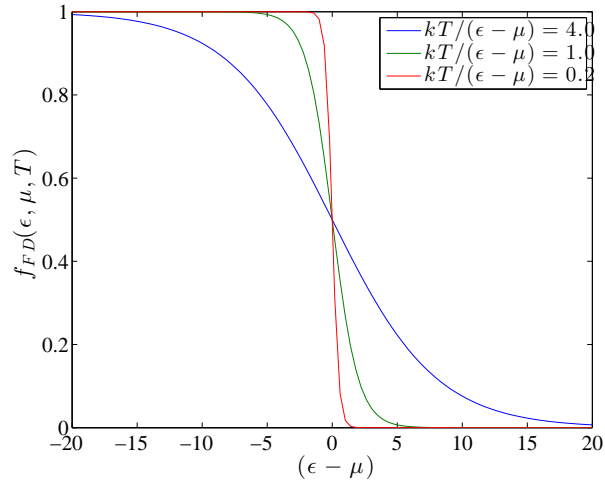
```
% Plot FD
x = linspace(-10,10);
f = 1.0./(exp(x)+1);
plot(x,f)
xlabel('\epsilon-\mu/kT');
ylabel('f')
```

and the results as shown in the figure:



We see that the function goes from 1 for low x to 0 for high x , and that the transition is over a region which size depends on kT . We see the effect of kT by plotting f as a function of $\epsilon - \mu$ for different values of kT with $kT = 0.1, 1.0,$ and $10.0 \cdot \epsilon - \mu$.

```
% Plot FD
ktvalues = [4.0 1.0 0.25];
legarray = [];
for i = 1:length(ktvalues)
    kt = ktvalues(i);
    x = linspace(-20,20);
    f = 1.0./(exp(x/kt)+1);
    plot(x,f)
    hold all
    legarray = [legarray; sprintf('kT/(\\epsilon-\\mu)=%3.1f',kt)];
end
xlabel('\epsilon-\mu');
ylabel('f_{FD}(\epsilon, \mu, T)');
legend(legarray);
```



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

$$\epsilon_F = \mu(T = 0) .$$

At $T = 0$ all the orbitals 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.

2.1 Bose-Einstein distribution

For Bosons more than one particle can be in the same orbital. The Gibbs sum and the average number of particles per orbital is then different than for Fermions.

Examples of bosons are photons, phonos, and particles such as Helium-4.

We find the number of particles in an orbital with energy ϵ using the Gibbs sum formalism.

The Gibbs sum is

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

and the average number of particles in this orbital is

$$\begin{aligned} \langle N \rangle &= \sum_N \sum_{s(N)} \frac{N}{Z_G} e^{-(\epsilon(N) - N\mu)/kT} \\ &= \frac{1}{Z_G} \sum_N N e^{-(\epsilon - \mu)N/kT} \\ &= \frac{1}{Z_G} \sum_N kT \frac{\partial}{\partial \mu} e^{-(\epsilon - \mu)N/kT} \\ &= \frac{\partial}{\partial \mu} kT \ln Z_G , \end{aligned}$$

where we have used a usual “trick” by introducing the derivative and taking it outside the sum.

The result is

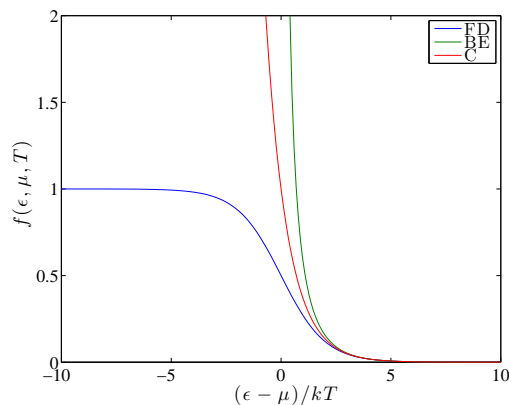
$$\langle N \rangle = f_{BE}(\epsilon, \mu, T) = \frac{1}{e^{(\epsilon - \mu)/kT} - 1} .$$

We have plotted the Bose-Einstein distribution along with the Fermi-Dirac distribution in the following figure:

```

% 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);

```



We see that the distribution diverges as ϵ approaches μ , that is, as $\epsilon - \mu$ approaches 0.

This means that as the temperature goes towards zero, all the particles will be in the ground state.

2.2 Classical limit

What happens in the high temperature (or low density) limit?

In the classical limit, we would demand that the number of atoms in an orbital is very small – hence there would not be any problems with particles being in the same orbital.

This means that the distribution function f also must be very small, $f \ll 1$, which in turn 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:

$$f(\epsilon, \mu, T) \simeq e^{(\epsilon-\mu)/kT} ,$$

We call this the **classical distribution function**.

We plotted this in the same plot, and see that it matches nicely for large values of $(\epsilon - \mu)/kT$.

How does this results pair up with our previous results for an ideal gas in the classical limit?

Our previous results were for a given number of particles, N , but our results now are for a given chemical potential. For a given chemical potential, μ , we can find the average number of particles as the sum of the (average) number of particles in each possible orbital, s , summed over all possible orbitals s :

$$N \simeq \langle N \rangle = \sum_s \langle N \rangle_s = \sum_s f(\epsilon_s, \mu, T) ,$$

In the classical limit, we have found that f has a simple form, so that the sum is:

$$N = \sum_s \exp((\epsilon_s - \mu)/kT) = e^{\mu/kT} \sum_s e^{\epsilon_s/kT} ,$$

where we recognize the sum as the one-particle partition function, Z_1 :

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

and the chemical potential therefore is:

$$\mu = kT \ln(N/Z_1) .$$

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

$$Z_1 = n_Q V ,$$

where

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

was called the quantum concentration. The chemical potential is therefore

$$\mu = kT \ln(N/(n_Q V)) = kT \ln(n/n_Q) .$$

3 Fermi gases

We can use a similar approach to determine the number of particle in a Fermi or a Boson gas – we know that the number of particles is given as the sum of the number of particles in each orbital:

$$N \simeq \langle N \rangle = \sum_s f(\epsilon_s, \mu, T) ,$$

where we find the (average) number of particles for a given μ . We could also assume that the number of particles is given, and that we want to find the chemical potential. How would we proceed?

Let us start at very low temperatures – or at $T = 0$. In this case, the Fermi distribution is a step function. All the states below the chemical potential are occupied by one particle, and none of the states above the chemical potential are occupied.

We call the chemical potential at $T = 0$ the Fermi energy for the system:

$$\epsilon_F = \mu(T = 0) .$$

For a given value of the Fermi energy, we can simply find the number of particles as the number of states with energies below (or at) the Fermi energy, because for all these states will be filled with exactly one particle.:

$$N \simeq \langle N \rangle = \sum_s f(\epsilon_s, \mu, T = 0) = \sum_{\epsilon_s \leq \epsilon_F} 1 .$$

We therefore need to find how the states are distributed in energy. The states for a single particle in a box of size $L \times L \times L$ are given as:

$$\epsilon(n_x, n_y, n_z) = \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \underbrace{\left(n_x^2 + n_y^2 + n_z^2\right)}_{n^2}.$$

Since at $T = 0$ all the states with energy less than ϵ_F are filled, this means that all the states with n_x, n_y, n_z less than some value n_F are filled, where n_F is

$$\epsilon_F = \frac{\hbar^2}{2m} \left(\frac{\pi n_F}{L}\right)^2$$

In n -space we have a uniform density of states: For each integer value of $n_x, n_y,$ and n_z we have two states (corresponding to spin up and spin down for spin 1/2 systems). The number of states with energy below ϵ_F , which corresponds to the number of states with n below n_F therefore correspond to two times the volume of 1/8 of a sphere in the n -space. And since each of these states are occupied by a particle at $T = 0$, this also corresponds to the number of particles:

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

which finally gives us a value for n_F :

$$n_F = \left(\frac{3N}{\pi}\right)^{1/3},$$

we can insert this into the equation for the Fermi energy, ϵ_F , getting:

$$\epsilon_F = \frac{\hbar^2}{2m} \left(\frac{\pi \left(\frac{3N}{\pi}\right)^{1/3}}{V^{1/3}}\right)^3 = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V}\right)^{2/3} = \frac{\hbar^2}{2m} (3\pi^3 n)^{2/3}.$$

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

We can also find the (internal) energy of the system. The contribution to the energy from state s is the energy of state s multiplied by the number of particles in state s . To find the total energy, we sum over all states:

$$\langle U \rangle = \sum_s \epsilon_s \langle N \rangle_s = \sum_s \epsilon_s f(\epsilon_s, \mu, T).$$

When $T = 0$, all states with energies below ϵ_F are occupied by one particle:

$$f(\epsilon_s, \epsilon_F, T = 0) = \begin{cases} 1 & \epsilon_s \leq \epsilon_F \\ 0 & \epsilon_s > \epsilon_F \end{cases}.$$

The energy is therefore found from the sum of states up to the Fermi energy:

$$\langle U \rangle = \sum_{\epsilon_s \leq \epsilon_F} \epsilon_s,$$

which we can also formulate as a sum over all possible values of n_x, n_y, n_z for $n \leq n_F$:

$$\langle U \rangle = 2 \cdot \sum_{n \leq n_F} \frac{\hbar^2}{2m} \left(\frac{\pi n}{L}\right)^2 n^2,$$

where the factor 2 is included to account for two quantum states (spin up and down) for each value in n -space.

We replace the sum over all values of \vec{n} to an integral over n :

$$\begin{aligned}
\langle U \rangle &= 2 \cdot \frac{1}{8} \cdot \int_0^{n_F} \epsilon(n) 4\pi n^2 dn \\
&= \frac{\pi^3}{2m} \left(\frac{\hbar}{L} \right)^2 \int_0^{n_F} n^4 dn \\
&= \frac{\pi^3}{10m} \left(\frac{\hbar}{L} \right)^2 n_F^5 \\
&= \frac{\pi^3}{10m} \left(\frac{\hbar}{L} \right)^2 n_F^5 \\
&= \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 n_F^2 \cdot \frac{\pi}{3} n_F^3 \cdot \frac{3}{5} \\
&= \epsilon_F \cdot N \cdot \frac{3}{5} \\
&= \frac{3}{5} N \epsilon_F .
\end{aligned}$$

We notice some properties of this solution: If we keep N constant and decrease V , we see that ϵ_F increases and hence U increases – as expected – this gives rise to a repulsion due to Fermi-exclusion.

3.1 Density of states

So far we have described the system in n -space where the density of states – the number of states per unit “volume” in n -space is uniform: The number of states in a volume from x, y, z to $x + dx, y + dy, z + dz$ is

$$D(n_x, n_y, n_z) dx dy dz$$

where $D(n_x, n_y, n_z) = 2$ is a constant. It is 2 because there are two spin states per value of $\vec{n} = (n_x, n_y, n_z)$.

We can similarly introduce a density of states in n -space – so that the number of states with magnitude n between n and $n + dn$

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

where the factor 2 again comes from the two spin states per \vec{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 – $f(\epsilon, \mu, T)$ – 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 \vec{n} which we convert to integrals of n (since all quantities only depend on the length of \vec{n} – and since the number of states is large so that the integral is a good approximation for the sum):

$$\langle N \rangle = \sum_{\vec{n}} 2f(\epsilon(n), \mu, T) = \int f(\epsilon(n), \mu, T) D(n) dn ,$$

and

$$\langle U \rangle = \sum_{\vec{n}} 2\epsilon(n) f(\epsilon(n), \mu, T) = \int \epsilon(n) f(\epsilon(n), \mu, T) D(n) dn ,$$

Now – we can perform this integral by inserting $\epsilon(n)$ into the equations. Or – we can change integration variable in the integral, and instead integrate over ϵ . That is, we introduce the variable $\epsilon(n)$ and the differential:

$$d\epsilon(n) = \frac{d\epsilon}{dn} dn ,$$

giving the integrals:

$$\langle N \rangle = \int f(\epsilon, \mu, T) D(n(\epsilon)) \frac{1}{d\epsilon/dn} d\epsilon ,$$

and

$$\langle U \rangle = \int \epsilon f(\epsilon, \mu, T) D(n(\epsilon)) \frac{1}{d\epsilon/dn} d\epsilon .$$

From these expressions we see that we can interpret

$$D(n(\epsilon)) \frac{1}{d\epsilon/dn} d\epsilon = D(\epsilon) d\epsilon ,$$

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

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:

$$D(n) dn = D(\epsilon) d\epsilon ,$$

and therefore

$$D(n(\epsilon)) \frac{1}{d\epsilon/dn} = D(\epsilon) ,$$

where we now use that

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

and therefore we find:

$$n = (\epsilon/a)^{1/2} ,$$

and that

$$\frac{d\epsilon}{dn} = 2an ,$$

which we insert in 3.1 to get

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

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 the following figure, where we have plotted both the density of states $D(\epsilon)$ and $f(\epsilon, \mu, T)$ in the same plot for three different temperatures, $T_0 = 0$ and for two finite temperatures, $T_1 < T_2$.

4 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 equilibrium 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 equilibrium). These waves can therefore have frequencies $f = c/\lambda$ and corresponding energies $\epsilon = nhf = n\hbar\omega$, 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:

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

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

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

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 (photons) in a box, the possible (standing wave) solutions are

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

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

$$\epsilon = pc = \hbar\omega = \frac{hcn}{2L},$$

instead of $\epsilon = p^2/2m$ 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:

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

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

$$\epsilon = \frac{hc}{2L} (n_x^2 + n_y^2 + n_z^2)^{1/2} = \frac{hcn}{2L}.$$

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:

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

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

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

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

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

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

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

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

We can also find the frequency (or energy, since they are propotional $\epsilon = h\nu$) 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 $\epsilon + d\epsilon$ – 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

$$U = \int_0^\infty \epsilon_n D(n) dn = \int_0^\infty \epsilon D(\epsilon) d\epsilon ,$$

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

$$\frac{U}{V} = \int_0^\infty \frac{\epsilon_n}{V} D(n) dn = \int_0^\infty \frac{\epsilon}{V} D(\epsilon) d\epsilon ,$$

which is what we just found above.

Starting from

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

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

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

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

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

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

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

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 $x = \epsilon/kT$.

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

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 be seen from the most prominent color – since the frequency of this color is proportional to the temperature. (If we can consider the body we examine as blackbody radiation).

4.1 Entropy of the photon gas

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

$$TdS = dU, \quad dS = \frac{dU}{T} = \frac{4aT^3}{T},$$

which we integrate from 0 to T , getting:

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

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

4.2 Radiation from a black body

What if we have a photon gas and we study the radiation emitted from a small hole 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

$$J = \frac{dE}{Adt} = \frac{udV}{Adt} = \frac{uAc dtg}{Adt} = ucg.$$

and

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

where σ is called the **Stefan-Boltzmann** 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).

5 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:

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

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

What happens when $\epsilon \ll kT$ 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 $\epsilon \gg kT$? 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 actually 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:

$$\epsilon_s = h\nu = \frac{hc_s}{\lambda} = \frac{hc_s n}{2L} ,$$

where L is the system size. Again n is the magnitude of the \vec{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:

$$f_{BE} = \frac{1}{e^{\epsilon/kT} - 1} .$$

We find the energy and the number of phonons by summing over all possible \vec{n} values:

$$U = 3 \sum_{n_x} \sum_{n_y} \sum_{n_z} \epsilon(\vec{n}) f(\epsilon, \mu = 0, T) .$$

The main difference with the crystal lattice is that not all values are possible – we can only have some values for \vec{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 a 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 $3N$:

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

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

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

and therefore that

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

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

$$U = \sum_{n_x} \sum_{n_y} \sum_{n_z} \epsilon_n f(\epsilon_n, \mu = 0, T) = \frac{3}{8} \int_0^{n_D} n^2 \frac{h\nu_n}{\exp(h\nu_n/kT) - 1} dn ,$$

where

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

The integral is therefore

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

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

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

where we call T_D the Debye temperature.

This gives – after some algebra:

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

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

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

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

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

and the heat capacity in this limit is

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

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 phonons and the contributions from the electrons, so that the heat capacity has the behavior:

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

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

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.

6 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

$$\epsilon = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2),$$

so that the lowest energy state has energy

$$\epsilon_0 = \frac{3h^2}{8mL^2},$$

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:

$$N_0 = \frac{1}{\exp((\epsilon_0 - \mu)/kT) - 1} ,$$

As the temperature approaches zero, we know that N_0 will be large, which means that $\exp((\epsilon_0 - \mu)/kT) - 1$ 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:

$$N_0 = \frac{1}{1 + (\epsilon_0 - \mu)/kT - 1} = \frac{kT}{\epsilon_0 - \mu} ,$$

and therefore that $\mu = \epsilon_0$ when $T = 0$ and then just a bit larger when T is small.

To make life simpler, let us change energy scales, so that $\epsilon_0 = 0$. The result is then

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

6.1 Spacing of levels

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

The energy is

$$\epsilon = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

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

$$\Delta\epsilon = \frac{3h^2}{8mL^2}$$

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

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

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?

6.2 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 level, N_0 , approaches N – all the particles are in the state with the lowest energy.

This means that

$$N_0 = \frac{1}{\exp((\epsilon_0 - \mu)/kT) - 1} ,$$

approaches N (which is very large) when $\mu \simeq \epsilon_0$.

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

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

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, $D(\epsilon)$:

$$N = N_0 + \int_{\epsilon_1}^{\infty} \frac{g(\epsilon)}{\exp((\epsilon - \mu)/kT) - 1} d\epsilon,$$

Since ϵ_1 also is very small ($\epsilon_1 \simeq 0$) and $g(0) = 0$, we can instead put 0 as the lower bound for the integral. In addition, we still assume that $\mu = 0$:

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

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

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

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

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

where the integral is

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

and therefore we find

$$N = N_0 + 2.612 \left(\frac{2\pi m k T}{h^2} \right)^{3/2} V.$$

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:

$$N = 2.612 \left(\frac{2\pi m k T_C}{h^2} \right)^{3/2} V,$$

which gives

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

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 :

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

which gives

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

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

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

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

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

which you now know how to solve.