

Thermal Physics of Bose & Fermi Gases

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Contents

1	Einsteins Model of a Solid	1
2	The Gibbs Factor	4
2.0.1	Example: CO Poisoning	7
2.1	My Grand Partition Function	7
3	Identical Particles	8
3.1	Distinguishable Particles	8
3.2	Indistinguishable Particles	8
3.3	Pauli Principle	8
4	The Bose-Einstein & Fermi-Dirac Distributions	9
4.1	Fermi-Dirac Distribution	10
4.2	Bose-Einstein Distribution	10
4.3	Spin Multiplicity	11
5	Classical Limit	11
5.1	Chemical Potential μ	12
5.1.1	Internal Energy & Heat Capacity	15
5.2	Entropy of an Ideal Gas	15
6	Fermi Gases	19

6.1	Ideal Fermi Gas at $T \approx 0$	20
6.2	Density of States	22
6.2.1	3D Density of States	23
6.2.2	Low T Corrections to N, U	29
6.3	Example: Electrons in Metals	32
6.4	Example: Liquid ${}^3\text{He}$	33
6.5	Example: Electrons in Stars	34
6.5.1	White Dwarf Stars	34
7	Bose Gases	38
7.1	Black Body Radiation	41
7.2	Spectral Energy Density	43
7.2.1	Pressure of a Photon Gas	45
8	Lattice Vibrations of a Solid	47
A	Colloquial Summary	I
B	Calculating the Density of States	IV
B.1	Energy Space: Non-Relativistic	IV
B.2	Energy Space: Ultra-Relativistic	V
C	Deriving FD & BE Distributions	VI

1 Einsteins Model of a Solid

Assume: each atom in a solid vibrates independantly about an equilibrium position. The vibrations are assumed to be simple harmonic, and all of the same frequency.

In a 3D solid, each atom can oscillate in 3 independant directions.
i.e. if N oscillators, then $\frac{N}{3}$ atoms.

Our system is a collection of N independant oscillators. Each oscillator has energy:

$$\left(n_i + \frac{1}{2}\right) \hbar\omega \quad (1.1)$$

Where n_i is the quantum number of the i^{th} oscillator: $n_i = 0, 1, 2, \dots$

ω = angular frequency of oscillator - remember they all have the same frequency.

Now, we proceed by measuring all energies relative to the ground state ($n_i = 0$). Hence:

$$\epsilon_i = n_i \hbar\omega \quad (1.2)$$

Where ϵ_i is the energy of the i^{th} oscillator.

Now, we have N such oscillators; so the total energy is:

$$U = (n_1 + n_2 + n_3 + \dots + n_N) \hbar\omega \quad (1.3)$$

$$= n \hbar\omega \quad (1.4)$$

Hence, n represents the energy of the system, in units of $\hbar\omega$.

The quantum state of the solid as a whole is specified by the list $(n_1, n_2, n_3, \dots, n_N)$.

Clearly, there are several quantum states corresponding to the same total energy. So, how many states can we have with a system of a particular energy?

Let $g(n, N)$ be the number of possible quantum states when the total energy is $n\hbar\omega$.

We can easily see/show that:

$$g(n, N) = \frac{(N + n - 1)!}{n!(N - 1)!} \quad (1.5)$$

The proof of which is trivial combinatorial arguments.

Now, the fundamental assumption is:

If a system is closed and in equilibrium, then it is equally likely to be in any of the accessible quantum states.

So, the probability of finding the system in a particular state is just:

$$\frac{1}{g(n, N)} \quad (1.6)$$

To summarise: $g(n, N)$ is the total number of quantum states. The probability that an Einstein solid is in any partiular state is given by $\frac{1}{g(n, N)}$. These ideas lead directly to the definitons & the

concept of entropy & 2nd law of thermodynamics.

To get an idea of temperature, we'll consider 2 Einstein solids connected to each other so that they can exchange energy.

U_A is the energy of solid $A = n_A \hbar \omega$.

U_B is the energy of solid $B = n_B \hbar \omega$.

Hence, the total energy is $U = U_A + U_B$; and is constant.

Now, the number of possible quantum states for $A + B$ is:

$$g_{A+B}(n, N) \tag{1.7}$$

$$N \equiv N_A + N_B \tag{1.8}$$

$$n \equiv n_A + n_B \tag{1.9}$$

Hence, N is the total number of oscillators, and n the total number of quanta. Then:

$$g_{A+B}(n, N) = \sum_{n_A} g(n_A, N_A) g(n - n_A, N - N_A) \tag{1.10}$$

Intuitively, we say that provided N_A and N_B are large enough, the system will settle down into a macrostate with $n_A = \tilde{n}_A$. Remarkably, this is already present in our analysis.

We claim that:

$$g_{A+B}(n, N) = \sum_{n_A \approx \tilde{n}_A} g(n_A, N_A) g(n_B, N_B) \tag{1.11}$$

To see this, pick $N_A = N_B = \frac{1}{2}N$, for simplicity. Now, using Stirling's approximation:

$$\ln n! \approx n \ln n - n \tag{1.12}$$

We can show that

$$g\left(\frac{1}{2}N, n_A\right) g\left(\frac{1}{2}N, n_B\right) \propto e^{-\frac{(n_A - \frac{1}{2}n)^2}{\sigma^2}} \tag{1.13}$$

Where we have defined the width of the Gaussian σ

$$\sigma^2 = \frac{n(N+n)}{2N} \tag{1.14}$$

This proof is done in Schroeder CH2.

If $n, N \gg 1$, then $\sigma \ll \frac{1}{2}n$. So, for example, if $N = n = 10^{22}$, then we have a $\sigma = 10^{11}$.

Hence, the equilibrium state is very well defined. i.e. $n_A = \frac{1}{2}n \pm \sigma = 10^{22} \pm 10^{11}$.

The cluster of macrostates around $n_A = \frac{1}{2}n$ have a much bigger statistical weight than all other macrostates, and by fundamental assumption, are much more likely. Now, we can locate the equilibrium configuration.

It occurs when $g_A g_B$ is a maximum. Hence, we have the differential:

$$d(g_A g_B) = 0 \tag{1.15}$$

$$\Rightarrow \frac{d}{dn_a} (g_A g_B) dn_a = 0 \tag{1.16}$$

$$\Rightarrow \frac{\partial g_A}{\partial n_a} g_B dn_a + \frac{\partial g_B}{\partial n_B} g_A dn_B = 0 \tag{1.17}$$

Now, we see that $dn_A = -dn_B$ (as n is fixed.) Hence, we have

$$g_B \frac{\partial g_A}{\partial n_A} - g_A \frac{\partial g_B}{\partial n_B} = 0 \quad (1.18)$$

$$\Rightarrow g_B \frac{\partial g_A}{\partial n_A} = g_A \frac{\partial g_B}{\partial n_B} \quad (1.19)$$

$$\frac{1}{g_A} \frac{\partial g_A}{\partial n_A} = \frac{1}{g_B} \frac{\partial g_B}{\partial n_B} \quad (1.20)$$

Hence, we find that something is equal in equilibrium.

We define temperature:

$$\frac{1}{k_B T} = \frac{1}{g} \frac{\partial g}{\partial U} \quad (1.21)$$

$$= \frac{\partial \ln g}{\partial U} \quad (1.22)$$

This definition gives T units of Kelvin, and according with our desire to have heat flow from hotter to cooler bodies.

Let a hotter body loose energy $\Delta U > 0$. Then, we can write (from (1.22)) as:

$$\Delta \ln g_{hot} = -\frac{\Delta U}{k_B T_{hot}} \quad (1.23)$$

$$\Delta \ln g_{cold} = -\frac{\Delta U}{k_B T_{cold}} \quad (1.24)$$

$$\Rightarrow \Delta \ln(g_{hot} \times g_{cold}) = \Delta \ln g_{hot} + \Delta \ln g_{cold} > 0 \quad (1.25)$$

Which should be so, as the system moves towards equilibrium. Thus:

$$\Delta \ln g_{hot} + \Delta \ln g_{cold} = \frac{\Delta U}{k_B} \left(\frac{1}{T_{cold}} - \frac{1}{T_{hot}} \right) \quad (1.26)$$

Which is > 0 if $T_{cool} < T_{hot}$.

The necessity that $\ln g$ increases as the system evolves towards the equilibrium state (*/equiv* state with maximum g) is just the second law of thermodynamics:

$$S = k_B \ln g \quad (1.27)$$

Where S is entropy. As we have that $\Delta \ln g > 0$, then this implies that $\Delta S > 0$. ‘Systems evolve to states of higher statistical weight’.

Aside The law of increase of entropy appears to signal a violation of time reversal invariance. This is not actually so: imagine molecules in a gas.

Although our discussion followed an Einstein solid, it should be clear that our discussion is of much broader generality.

So, so we have:

$$S = k_B \ln g \quad (1.28)$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} \quad (1.29)$$

Since we worked hard to get $g(n, N)$, we may as well make use of it. Lets predict the heat capacity of a solid.

$$\frac{S}{k_B} = \ln g \quad (1.30)$$

$$= (N + n) \ln(N + n) - n \ln n - N \ln N \quad (1.31)$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} \Rightarrow \frac{1}{T} = \frac{1}{\hbar\omega} \frac{\partial S}{\partial n} \quad (1.32)$$

$$\Rightarrow \ln\left(\frac{N + n}{n}\right) = \frac{\hbar\omega}{k_B T} \quad (1.33)$$

$$\Rightarrow n(T) = \frac{N}{e^{\frac{\hbar\omega}{k_B T}} - 1} \quad (1.34)$$

Hence, we have the energy of the solid as a function of temperature: $n(T)$; remembering that $U = n\hbar\omega$. Hence, we have that the specific heat capacity C is:

$$\begin{aligned} C &= \frac{\partial U}{\partial T} \\ &= \hbar\omega \frac{\partial n}{\partial T} \\ &= \frac{N\hbar\omega \frac{\hbar\omega}{k_B T^2} e^{\frac{\hbar\omega}{k_B T}}}{(e^{\frac{\hbar\omega}{k_B T}} - 1)^2} \\ &= \frac{Nk_B X^2 e^X}{(e^X - 1)^2} \quad X \equiv \frac{\hbar\omega}{k_B T} \end{aligned}$$

Hence, for $X \ll 1$ (i.e. high T), we have the Dulong-Petit law: $C = Nk_B$. For $X \gg 1$ (i.e. low T), we have that $C = Nk_B X^2 e^{-X}$. So, graphically, we have a curve, starting from 0 at 0, which increases to a constant at high temperatures.

2 The Gibbs Factor

We can go further (than the previously closed systems), and figure out the probability that a system is in a particular quantum state.

If the system is closed, then we know the answer: the probability of the system being in any one state is just $\frac{1}{g}$.

Generally however, we are interested in systems which are not isolated (i.e. are not closed).

Suppose we have a really really big box (denoted the 'reservoir' R), which is closed; and a smaller box (our system S), within R , and is allowed to exchange particles and energy with R .

At equilibrium, the total number of states available to the system as a whole is:

$$g_T = g_S \times g_R \quad (2.1)$$

Where g_i is the number of accesible states to the system i .

In equilibrium, g_T is a maximum. As $g_T(U_S, N_S)$ we can hence write its differential:

$$dg_T = 0 \quad (2.2)$$

$$= \frac{\partial g_T}{\partial U_S} dU_S + \frac{\partial g_T}{\partial N_S} dN_S \quad (2.3)$$

And, as $g_T \equiv g_R + g_S$, we use the product rule to get:

$$g_S \frac{\partial g_R}{\partial U_S} dU_S + g_R \frac{\partial g_S}{\partial U_S} dU_S + g_S \frac{\partial g_R}{\partial N_S} dN_S + g_R \frac{\partial g_S}{\partial N_S} dN_S = 0 \quad (2.4)$$

$$\Rightarrow \left(g_S \frac{\partial g_R}{\partial U_S} + g_R \frac{\partial g_S}{\partial U_S} \right) dU_S + \left(g_S \frac{\partial g_R}{\partial N_S} + g_R \frac{\partial g_S}{\partial N_S} \right) dN_S = 0 \quad (2.5)$$

Now, using $dU_S = -dU_R$ and $dN_S = -dN_R$, we have:

$$\frac{1}{g_R} \frac{\partial g_R}{\partial U_R} = \frac{1}{g_S} \frac{\partial g_S}{\partial U_S} \quad (2.6)$$

$$\frac{1}{g_R} \frac{\partial g_R}{\partial N_R} = \frac{1}{g_S} \frac{\partial g_S}{\partial N_S} \quad (2.7)$$

Now, (2.6) gives us the previous definition of temperature: $T_R = T_S$ in equilibrium. The other equation, (2.7) will give us that the chemical potential is the same in equilibrium:

$$\mu_R = \mu_S \quad (2.8)$$

$$\mu \equiv -T \frac{\partial S}{\partial N} = -\frac{T k_B}{g} \frac{\partial g}{\partial N} \quad (2.9)$$

As $S = k_B \ln g$, we have that $\frac{\partial S}{\partial N} = \frac{1}{g} \frac{\partial g}{\partial N}$.

So far, we have assumed that the volume of our system is constant. If this is not the case, all we have, is that $g(U, N, V)$, and hence an added term of $\frac{\partial g}{\partial V} dV$ (for both S, R) in (2.5). This will give us, that in equilibrium, we have:

$$\frac{1}{g_R} \frac{\partial g_R}{\partial V_R} = \frac{1}{g_S} \frac{\partial g_S}{\partial V_S} \quad (2.10)$$

Which leads us to give the definition of pressure:

$$p = T \frac{\partial S}{\partial V} \quad (2.11)$$

And that $p_S = p_R$ in equilibrium.

Now, our goal is to find $P(N_S, U_S)$, the probability to find the system in a particular quantum state. i.e. $g_S = 1$.

So,

$$P(N_S, U_S) \propto g_R(N_T - N_S, U_T - U_S) \times 1 \quad (2.12)$$

$$\Rightarrow P(N_S, U_S) \propto \exp\left(\frac{S_R(N_T - N_S, U_T - U_S)}{k_B}\right) \quad (2.13)$$

Now, we Taylor expand around (N_T, U_T) , giving:

$$S_R(N_T - N_S, U_T - U_S) = S_R(N_T, U_T) - N_S \frac{\partial S_R}{\partial N} - U_S \frac{\partial S_R}{\partial U} \quad (2.14)$$

$$= S_R(N_T, U_T) + \frac{N_S \mu}{T} - \frac{U_S}{T} \quad (2.15)$$

Neglecting terms in higher differentials, as reservoir is big enough, then its temperature T and chemical potential μ are independent of N_S, U_S . So, we have:

$$P(N_S, U_S) \propto \exp\left(\frac{S_R(N_T, U_T)}{k_B} + \frac{N_S \mu}{k_B T} - \frac{U_S}{k_B T}\right) \quad (2.16)$$

Now, we notice that the first term in the exponential is a constant (or assumed to be so constant that it is!); also, we now drop the subscripts, and write that $U_S = \epsilon_S = \epsilon$. This gives us:

$$P(N, \epsilon) \propto \exp\left(\frac{N\mu - \epsilon}{k_B T}\right) \quad (2.17)$$

Which is known as the **Gibbs distribution function**.

Notice, that if N is fixed, then the $\frac{N\mu}{k_B T}$ term is another constant, and we have that:

$$P(\epsilon) \propto \exp\left(-\frac{\epsilon}{k_B T}\right) \quad (2.18)$$

Which is the **Boltzmann distribution function**, we saw last year.

To use the probability properly, we must normalise it. That is:

$$\sum_N \sum_{\epsilon} P(N, \epsilon) = 1 \quad (2.19)$$

So, to do this, we define the **grand partition function** \mathcal{Z} :

$$\mathcal{Z}(\mu, T) \equiv \sum_N \sum_{\epsilon} \exp\left(\frac{N\mu - \epsilon}{k_B T}\right) \quad (2.20)$$

So that we now have the probability to find the system as a whole, in a particular state with energy ϵ , and number of particles N , is given by:

$$P(N, \epsilon) = \frac{\exp\left(\frac{N\mu - \epsilon}{k_B T}\right)}{\mathcal{Z}} \quad (2.21)$$

Note, if the system has more than one type of particle, then the exponent changes thus:

$$\exp\left(\frac{N\mu - \epsilon}{k_B T}\right) \rightarrow \exp\left(\frac{N_1\mu_1 + N_2\mu_2 + \dots - \epsilon}{k_B T}\right) \quad (2.22)$$

We can compute the average, in the usual way:

$$\langle X \rangle = \sum P_i X_i \quad (2.23)$$

$$= \sum_{N, \epsilon} \frac{\exp\left(\frac{N\mu - \epsilon}{k_B T}\right)}{\mathcal{Z}} X(N, \epsilon) \quad (2.24)$$

2.0.1 Example: CO Poisoning

Suppose that our system of interest is a Haemoglobin molecule, in one of 3 states: unbound (1); bound to O_2 (2); bound to CO (3).

So, we can write the particle numbers, for each state, in terms of $(N_{Hb}, N_{O_2}, N_{CO})$, with their associated energies (given)

- (1) : (1, 0, 0) $\epsilon_1 = 0$
- (2) : (1, 1, 0) $\epsilon_2 = -0.7eV$
- (3) : (1, 0, 1) $\epsilon_3 = -0.85eV$

The chemical potentials are: μ_{Hb} = dont care! $\mu_{O_2} = -0.6eV$, $\mu_{CO} = -0.7eV$ (again, values given). $T = 310K$.

So, to calculate \mathcal{Z} , we have:

$$\mathcal{Z} = \exp\left(\frac{N_1^{Hb}\mu^{Hb} + N_1^{O_2}\mu^{O_2} + N_1^{CO}\mu^{CO} - \epsilon_1}{k_B T}\right) \quad (2.25)$$

$$+ \exp\left(\frac{N_2^{Hb}\mu^{Hb} + N_2^{O_2}\mu^{O_2} + N_2^{CO}\mu^{CO} - \epsilon_2}{k_B T}\right) \quad (2.26)$$

$$+ \exp\left(\frac{N_3^{Hb}\mu^{Hb} + N_3^{O_2}\mu^{O_2} + N_3^{CO}\mu^{CO} - \epsilon_3}{k_B T}\right) \quad (2.27)$$

$$= e^{\mu_{Hb}/k_B T} + e^{(\mu_{Hb} + \mu_{O_2} + 0.7eV)/k_B T} + e^{(\mu_{Hb} + \mu_{CO} + 0.85eV)/k_B T} \quad (2.28)$$

$$= 161 \quad (2.29)$$

Hence, we can write what the probability of each state (1), (2) or (3) is, of occurring:

- (1): Hb is unbound: $P_1 = \frac{e^{\mu_{Hb}/k_B T}}{\mathcal{Z}} = \frac{1}{161}$.
- (2): Hb is bound to O_2 : $P_2 = \frac{e^{(\mu_{Hb} + \mu_{O_2} + 0.7eV)/k_B T}}{\mathcal{Z}} = \frac{40}{161} = 25\%$.
- (3): Hb is bound to CO : $P_3 = \frac{e^{(\mu_{Hb} + \mu_{CO} + 0.85eV)/k_B T}}{\mathcal{Z}} = \frac{120}{161} = 75\%$

2.1 My Grand Partition Function

I find the following formula easier to use, to write the probability of finding the system in a state with energy ϵ_j , with N particles:

$$P(N, \epsilon_j) = \frac{e^{\epsilon_j/kT} \prod_i e^{N_i \mu_i/kT}}{\mathcal{Z}}$$

Thus, the grand partition function \mathcal{Z} is the sum over all possible energy states as well:

$$\mathcal{Z} = \sum_j e^{\epsilon_j/kT} \prod_i e^{N_i \mu_i/kT}$$

3 Identical Particles

We shall be looking at cases where the ‘system’ is a ‘bunch of particles’. We need to be able to count quantum states for such system. We start with a simple system.

3.1 Distinguishable Particles

If we have 2 distinguishable particles (A, B) , and 2 accesible quantum states (ϵ_1, ϵ_2) , and if the particles are distinguishable, then we can have 4 configurations: $(AB, 0), (0, AB), (A, B), (B, A)$. Hence, 4 allowed states of the system.

3.2 Indistinguishable Particles

If we have again 2 accesible states, but 2 identical particles, we now have that the possible configurations are: $(AA, 0), (0, AA), (A, A)$. Hence, 3 allowed states. This is the case if we allow the two particles to be in the same state at the same time, We denote these types of particles **bosons**.

The other possibility is that we dont allow the two particles to be in the same state. Hence, we have that the only configuration is (A, A) . We denote these types of particles **fermions**. That there is only one state allowed, is a consequence of the Pauli Principle. Which we shall now derive.

3.3 Pauli Principle

Let $\phi_i(x)$ be an energy eigenstate for a single particle in the system, so that:

$$\hat{H}(x)\phi_i(x) = E_i\phi_i(x)$$

If our two particles do not interact, then $\phi_i(x)\phi_j(y)$ is an energy eigenstate of the two particle system, with $E = E_i + E_j$:

$$\left[\hat{H}(x) + \hat{H}(y) \right] \phi_i(x)\phi_j(y) = E_i\phi_i(x)\phi_j(y) + E_j\phi_i(x)\phi_j(y)$$

If the particles are indistinguishable, then no observable can depend upon which particle is where. Hence, we have that observables should be unchanged if we swap the positions $x \leftrightarrow y$:

$$\langle \hat{O} \rangle = \int \psi^*(x, y) \hat{O}(x, y) \psi(x, y) d\tau$$

Should be unchanged under the swap.

Recall that any linear combination of 2 eigenstates is also an eigenstate with the same eigenvalue. So, we want a linear combination:

$$\begin{aligned} a\phi_i(x)\phi_j(y) + b\phi_i(y)\phi_j(x) &= \psi_{ij}(x, y) \\ \Rightarrow \left[\hat{H}(x) + \hat{H}(y) \right] \psi_{ij}(x, y) &= (E_i + E_j)\psi_{ij}(x, y) \end{aligned}$$

Now, we want:

$$|\psi_{ij}(x, y)|^2 = |\psi_{ij}(y, x)|^2$$

This implies that:

$$\psi_{ij}(x, y) = e^{i\alpha} \psi_{ij}(y, x)$$

Where swapping over the spatial coordinates has the effect of picking up some phase $e^{i\alpha}$. Now, if we swap back:

$$\begin{aligned}\psi_{ij}(x, y) &= e^{i\alpha} e^{i\alpha} \psi_{ij}(x, y) \\ \Rightarrow e^{2i\alpha} &= 1 \\ \Rightarrow e^{i\alpha} &= \pm 1\end{aligned}$$

So, we have that:

$$\psi_{ij}(x, y) = \pm \psi_{ij}(y, x)$$

Now, there are two linear combinations of $\phi_i(x)\phi_j(y)$ and $\phi_i(y)\phi_j(x)$ which satisfy this requirement:

$$\psi_{ij}(x, y) = \phi_i(x)\phi_j(y) \pm \phi_i(y)\phi_j(x) \quad (3.1)$$

If the positive sign is taken, then the wavefunction is symmetric (under interchange of two identical particles). We classify this type as being bosons. If the negative sign is taken, then the wavefunction is anti-symmetric, and we classify these as fermions.

We see that the Pauli principle is a direct consequence of the symmetry property for fermions:

If we have 2 identical fermions in the same state i , then:

$$\begin{aligned}\psi_{ii}(x, y) &= \phi_i(x)\phi_i(y) - \phi_i(y)\phi_i(x) = 0 \\ \Rightarrow |\psi_{ii}(x, y)|^2 &= 0\end{aligned}$$

That is, there is no probability for the system to be found in such a state. Therefore, two identical fermions can not be in the same quantum state. There is no such problem for bosons.

This is actually a pretty weird conclusion. If we have the idea that an electrons wavefunction is never zero (just really small) anywhere, then any two electrons in the universe must be considered dependantly, and we must conclude that these two electrons can never be in the exact same state. That is, we cannot treat an electron sitting on the earth independantly to one on the other side of the galaxy. These two electrons simply can never be in the same state. We end up concluding that they are allowed to sit very very close to being in the same state, but not quite. This can be shown in potential well arguments. There is a very fine difference between the ground state of two electrons whose wavefunctions overlap.

We ought to conclude by stating that bosons have integer spin, and fermions half-integer. This is proved using relativistic quantum mechanics, and is hard to do!

If a collection of particles have an odd number of fermions, then the system is fermionic; even number of fermions gives a bosonic system.

4 The Bose-Einstein & Fermi-Dirac Distributions

We now focus on an ideal gas of fermions or bosons.

We recall that the Gibbs distribution gives the probability to find the system S in a single quantum

state.

A single state of S is specified by the set $\{n_i, \epsilon_i\}$; where n_i is the number of particles in the energy level ϵ_i . So:

$$P(\{n_i, \epsilon_i\}) = \frac{\exp[\mu(n_1 + n_2, + \dots)/kT - (\epsilon_1 n_1 + \epsilon_2 n_2 + \dots)/kT]}{\sum_{n_1, n_2, \dots} \exp[\mu(n_1 + n_2, + \dots)/kT - (\epsilon_1 n_1 + \epsilon_2 n_2 + \dots)/kT]} \quad (4.1)$$

$$= \frac{e^{n_1(\mu - \epsilon_1)/kT} e^{n_2(\mu - \epsilon_2)/kT} \dots}{\sum_{n_1} e^{n_1(\mu - \epsilon_1)/kT} \sum_{n_2} e^{n_2(\mu - \epsilon_2)/kT} \dots} \quad (4.2)$$

$$= P_1(n_1) P_2(n_2) \dots \quad (4.3)$$

Where:

$$P_i(n_i) \equiv \frac{e^{n_i(\mu - \epsilon_i)/kT}}{\sum_{n_i} e^{n_i(\mu - \epsilon_i)/kT}}$$

Thus, $P_i(n_i)$ is the probability to find n_i particles in energy level ϵ_i . What we have done is to show that the probability to find the system in a particular state is just the product of the probabilities of finding a particular number of particles in the particular state.

Now, we can figure out the mean number of particles in a particular energy level:

$$\langle n(\epsilon_i) \rangle = \sum P_i n_i$$

It is the calculation of this sum which we now consider:

4.1 Fermi-Dirac Distribution

Here, we just consider the fermionic case. We know that we can only have either one or zero particles in each state. Thus, the sum over n is just for $n = 0, 1$. Hence:

$$\langle n(\epsilon) \rangle_{FD} = \sum_{n=0,1} P(n) n \quad (4.4)$$

$$= \frac{1 \times 0 + e^{(\mu - \epsilon)/kT}}{1 + e^{(\mu - \epsilon)/kT}} \quad (4.5)$$

$$= \frac{1}{1 + e^{(\epsilon - \mu)/kT}} \quad (4.6)$$

$$\Rightarrow \langle n(\epsilon) \rangle_{FD} = \frac{1}{1 + e^{(\epsilon - \mu)/kT}} \quad (4.7)$$

Where $\langle n(\epsilon) \rangle_{FD}$ is called the **Fermi-Dirac Distribution**.

4.2 Bose-Einstein Distribution

Here, we can have any number of particles in each state. Hence:

$$\langle n(\epsilon) \rangle_{BE} = \frac{0 + e^{(\mu - \epsilon)/kT} + 2e^{2(\mu - \epsilon)/kT} + \dots}{1 + e^0 + e^{20} + \dots} \quad (4.8)$$

Now, if we define:

$$a \equiv e^{(\mu-\epsilon)/kT}$$

We see that the denominator is a geometric series:

$$1 + a + a^2 + a^3 + \dots = \frac{1}{1-a}$$

And that the top is:

$$a + 2a^2 + 3a^3 + \dots \tag{4.9}$$

$$= a(1 + 2a + 3a^2 + \dots) \tag{4.10}$$

$$= a\left(\frac{d}{da}(1 + a + a^2 + \dots)\right) \tag{4.11}$$

$$= \frac{a}{(1-a)^2} \tag{4.12}$$

Hence, we have that:

$$\langle n(\epsilon) \rangle_{BE} = \frac{\frac{a}{(1-a)^2}}{\frac{1}{1-a}} \tag{4.13}$$

$$= \frac{1}{\frac{1}{a} - 1} \tag{4.14}$$

$$= \frac{1}{e^{(\epsilon-\mu)/kT} - 1} \tag{4.15}$$

$$\Rightarrow \langle n(\epsilon) \rangle_{BE} = \frac{1}{e^{(\epsilon-\mu)/kT} - 1} \tag{4.16}$$

Where $\langle n(\epsilon) \rangle_{BE}$ is called the **Bose-Einstein Distribution**.

4.3 Spin Multiplicity

In a gas of particles with spin s , the mean number of particles per state is hence given by:

$$\langle n(\epsilon) \rangle = \frac{2s + 1}{e^{(\epsilon-\mu)/kT} \pm 1}$$

5 Classical Limit

We have the classical limit when:

$$\langle n(\epsilon) \rangle \ll 1 \quad \forall \epsilon$$

i.e. we have that:

$$\langle n(\epsilon) \rangle \approx \exp\left(\frac{\mu - \epsilon}{kT}\right)$$

Using the approximation, we can start to calculate things.

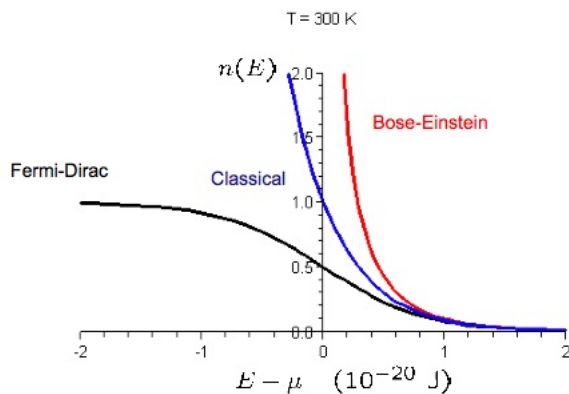


Figure 1: Graph showing how the three distributions change. Notice that the Fermi-Dirac distribution stays below 1.

5.1 Chemical Potential μ

We can develop insight into μ by computing the mean number of particles in our system as a whole. Suppose we have N particles, within a big cube, with sides length L . Our system is within the big cube. So, we have:

$$\begin{aligned} N &= \sum_i \langle n(\epsilon_i) \rangle \\ &= \sum_i \exp\left(\frac{\mu - \epsilon}{kT}\right) \end{aligned}$$

Now, let us attempt the summation.

We need the single particle energy levels for (non-interacting) particles in a box of side L . To do this, just solve the Schrodinger equation, to find:

$$\epsilon(n_1, n_2, n_3) = \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2)$$

Where the integers n_i run from $1, 2, 3, \dots, \infty$. Hence we have that the total number of particles in the system is:

$$N = \sum_{n_1, n_2, n_3} \exp\left(\frac{\mu - \epsilon(n_1, n_2, n_3)}{kT}\right)$$

To find typical values of n_1, n_2, n_3 via noting that we have that $\epsilon = kT$; hence:

$$n_1^2 + n_2^2 + n_3^2 \approx \frac{kT 2mL^2}{\hbar^2 \pi^2}$$

Now, if $L = 1m$ & $m = 10^{-26}kg$, we have that $n_1, n_2, n_3 \approx 10^{19/2}$.

Going back to evaluation of the summation: As we find that $n_i \gg 1$, we will make the approximation of making the energy levels continuous:

$$\sum_{n_1, n_2, n_3} \exp\left(\frac{\mu - \epsilon(n_1, n_2, n_3)}{kT}\right) \approx \int \int \int dn_1 dn_2 dn_3 \exp\left(\frac{\mu - \epsilon(n_1, n_2, n_3)}{kT}\right)$$

So, we have that:

$$\begin{aligned} N &\approx \int_0^\infty dn_1 \int_0^\infty dn_2 \int_0^\infty dn_3 e^{\mu/kT} e^{-\frac{\hbar^2 \pi^2 n_1^2}{2mL^2 kT}} e^{-\frac{\hbar^2 \pi^2 n_2^2}{2mL^2 kT}} e^{-\frac{\hbar^2 \pi^2 n_3^2}{2mL^2 kT}} \\ &= e^{\mu/kT} \left[\int_0^\infty dn e^{-\alpha n^2} \right]^3 \quad \alpha \equiv \frac{\hbar^2 \pi^2}{2mL^2 kT} \end{aligned}$$

Now, the integral is given by:

$$\int_0^\infty dx e^{-\alpha x^2} = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}}$$

Hence:

$$\begin{aligned} N &\approx \frac{e^{\mu/kT}}{2} \sqrt{\frac{\pi}{\alpha}} \\ &= \exp\left(\frac{\mu}{kT}\right) \left(\frac{1}{2} \sqrt{\frac{2mL^2 kT}{\hbar^2 \pi}}\right)^3 \end{aligned}$$

Rearranging, we get:

$$\mu = kT \ln\left(\frac{n}{n_Q}\right) \quad (5.1)$$

Where we have defined the number density & quantum density:

$$n \equiv \frac{N}{V} \quad (5.2)$$

$$n_Q \equiv \left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2} \quad (5.3)$$

So, we have managed to define the chemical potential in terms of density quantities; i.e. local quantities, independent of the big box.

Notice, for classical limit, we have that $e^{(\epsilon-\mu)/kT} \gg 1$. Thus, as $\epsilon \approx kT$, we have that μ must be ‘very negative’; hence in (5.1), this corresponds to $n_Q \gg n$ for classical physics; and $n > n_Q$ for quantum physics.

Thus, the classical limit occurs when the system has a low density (n small) and/or high temperature (T large).

And quantum physics becomes important for high density (n large) and/or low temperatures (T small).

We can estimate n_Q by assuming it to be equal to the concentration when each particle occupies a volume λ_Q^3 , where λ_Q is the de Broglie wavelength.

Now, we have that $\lambda_Q p = h$, and that $E \approx kT \Rightarrow \frac{p^2}{2m} \approx kT$, for non-relativistic. Hence, estimating

gives: $p \approx \sqrt{mkT}$. Therefore, $\lambda_Q \approx \frac{h}{\sqrt{mkT}}$. Now, we want $n_Q \approx \frac{1}{\lambda_Q^3}$, and we have hence achieved the previous value of n_Q .

Hence, we may say that the quantum density n_Q is that at which particles occupy boxes the size of their de Broglie wavelengths.

Comments

- Don't forget the spin multiplicity factor. If the gas particles have spin s , then $n = (2s + 1) \exp(\mu/kT) n_Q \Rightarrow \mu = kT \ln(n/(2s + 1)n_Q)$.
- Actual values of μ depend of what we choose as the zero of the energy scale. If $\epsilon = \epsilon_0 + \epsilon(n_1, n_2, n_3)$, then a change of $\mu \rightarrow \mu + \epsilon_0$ would keep everything the same. So $\mu = \epsilon_0 + kT \ln(n/n_Q)$.

We have assumed that the gas so far is monoatomic. Now, if we give the system a set $\{j\}$ of internal quantum numbers (e.g angular momentum), then we have that we can find the new chemical potential μ . We proceed by finding the average number of particles (in total) in the system, which is just the sum over probabilities to find a number of particles in an energy state:

$$\begin{aligned}
 N &= \sum_i n_i \\
 &= \sum_i e^{\frac{\mu - \epsilon_i}{kT}} \\
 &= e^{\mu/kT} \sum_i e^{-\epsilon_i/kT} \\
 &= e^{\mu/kT} Z \\
 &= \frac{n}{n_Q} Z
 \end{aligned}$$

Where we have defined the partition function $Z \equiv \sum_i e^{-\epsilon_i/kT}$. Now, from the definition $n = \frac{N}{L^3}$. Hence:

$$N = \frac{NZ}{L^3 n_Q} \tag{5.4}$$

$$\Rightarrow Z = n_Q L^3 \tag{5.5}$$

So, now, if we introduce internal degrees of freedom, we introduce another energy term ϵ_j ; hence:

$$\begin{aligned}
 N &= e^{\mu/kT} \sum_i e^{-\epsilon_i/kT} \sum_j e^{-\epsilon_j/kT} \\
 \Rightarrow n = \frac{N}{L^3} &= e^{\mu/kT} \frac{\sum_i e^{-\epsilon_i/kT}}{L^3} \sum_j e^{-\epsilon_j/kT} \\
 \Rightarrow n &= e^{\mu/kT} \frac{Z}{L^3} Z_{int} \\
 \Rightarrow \mu &= kT \ln \left(\frac{n}{n_Q Z_{int}} \right)
 \end{aligned}$$

Hence, we see that if we introduce internal motion of the particles, described by the internal partition function Z_{int} , the chemical potential is given by:

$$\mu = kT \ln \left(\frac{n}{n_Q Z_{int}} \right) \quad (5.6)$$

5.1.1 Internal Energy & Heat Capacity

We know that the internal energy U is given by the sum over the different states, where each state is the mean number of particles in each energy level (state):

$$\begin{aligned} U &= \sum_i \langle n_i \rangle \epsilon_i \\ &= \sum_i e^{(\mu - \epsilon_i)/kT} \epsilon_i \\ &= e^{\mu/kT} \sum_i e^{-\epsilon_i/kT} \epsilon_i \\ &= \frac{n}{n_Q} \sum_i e^{-\epsilon_i/kT} \epsilon_i \\ &= \frac{N}{L^3} \frac{L^3}{Z} \sum_i e^{-\epsilon_i/kT} \epsilon_i \\ &= \frac{N}{Z} \sum_i e^{-\epsilon_i/kT} \epsilon_i \end{aligned}$$

Where we have used that $Z = n_Q L^3$ and $n = N/L^3$. Now, we notice that the last expression is equal to the differential of the logarithm of the partition function:

$$\begin{aligned} \Rightarrow U &= NkT^2 \frac{\partial \ln Z}{\partial T} \\ &= NkT^2 \frac{\partial}{\partial T} \ln(n_Q L^3) \\ &= \frac{3}{2} NkT \end{aligned}$$

After doing the differentiation, and subbing in for n_Q .

We can also compute the heat capacity:

$$C_V = \frac{\partial U}{\partial T} = \frac{3}{2} Nk$$

Where we have now been able to reproduce last years results.

5.2 Entropy of an Ideal Gas

We must count all accesible quantum states. But it is not clear how to do that for a system with variable particle number and energy.

We can compute the mean entropy by considering the following situation:

Suppose we have a big box, and inside the big box is m little boxes. One of these little boxes is our ‘system’. Hence, our system is surrounded by $(m - 1)$ replica systems, all in thermal and diffusive equilibrium with each other. Each system is specified by specifying its quantum state.

Each distinct configuration of the boxes corresponds to 1 quantum state of the entire system (where the entire system is the collection of m little boxes).

To compute the entropy of the entire system, we just need to count the number of ways of shuffling the boxes. This is just:

$$W = \sum_{m_1, m_2, \dots} \frac{m!}{m_1! m_2! \dots} = m! \sum_{m_1, m_2, \dots} \frac{1}{m_1! m_2! \dots}$$

Where we have that m_i is the number of boxes in state i .

Hence, the entropy of the complete system is:

$$\begin{aligned} S_m &= k \ln W \\ &= k \left(m \ln m - \sum_i m_i \ln m_i \right) \end{aligned}$$

Where we have used Stirling’s approximation, and noting that $\sum_i m_i = m$. Hence, we see that:

$$m \ln m = \sum_i m_i \ln m$$

Therefore:

$$\begin{aligned} S_m &= k \sum_i m_i \ln \frac{m}{m_i} \\ &= -km \sum_i \frac{m_i}{m} \ln \frac{m_i}{m} \end{aligned}$$

But, as we have that $m \rightarrow \infty$, so we have that:

$$\frac{m_i}{m} = \text{fraction of all boxes in } i^{\text{th}} \text{ state} = p_i$$

Where p_i is just the previous Gibbs factor:

$$p_i = \frac{e^{(\mu N_i - \epsilon_i)/kT}}{\sum e^{(\mu N_i - \epsilon_i)/kT}}$$

Where the sum is over all microstates of the system.

Therefore, we have derived that:

$$S = -k_B \sum_i p_i \ln p_i \tag{5.7}$$

Where we have made no distinction between classical or quantum gases: this holds for both.

So, for an ideal gas, we have that:

$$p_i = \frac{e^{(\mu N_i - E_i)/kT}}{\mathcal{Z}}$$

Where we have that:

$$\begin{aligned} N_i &= n_1 + n_2 + n_3 + \dots \\ E_i &= n_1\epsilon_1 + n_2\epsilon_2 + n_3\epsilon_3 + \dots \end{aligned}$$

Hence, let us compute \mathcal{Z} generally.

$$\mathcal{Z} = \sum_{\{n_i\}} e^{n_1(\mu-\epsilon_1)/kT} \times e^{n_2(\mu-\epsilon_2)/kT} \times \dots$$

Where we have a summation over occupancies over single particle states. Hence, we can show that this summation is the same as the product of the corresponding factors:

$$\mathcal{Z} = \prod_{\{\epsilon_i\}} \left(1 + e^{(\mu-\epsilon_i)/kT} + e^{2(\mu-\epsilon_i)/kT} + \dots \right) \quad (5.8)$$

$$= \prod_{\{\epsilon_i\}} \sum_{\{n_j\}} \left(e^{n_j(\mu-\epsilon_i)/kT} \right) \quad (5.9)$$

And we see that the sum is just the standard $\sum_{i=0}^{\infty} x^i = \frac{1}{1-x}$, to give:

$$\mathcal{Z} = \prod_{\{\epsilon_i\}} \frac{1}{1 - e^{(\mu-\epsilon_i)/kT}}$$

Taking the logarithm:

$$\begin{aligned} \ln \mathcal{Z} &= \ln \prod_{\{\epsilon_i\}} \frac{1}{1 - e^{(\mu-\epsilon_i)/kT}} \\ &= \sum_{\{\epsilon_i\}} \ln \frac{1}{1 - e^{(\mu-\epsilon_i)/kT}} \\ &= - \sum_{\{\epsilon_i\}} \ln 1 - e^{(\mu-\epsilon_i)/kT} \end{aligned}$$

Hence, we see that, for bosons, this sum is unrestricted; so:

$$\ln \mathcal{Z}^{boson} = - \sum_{\{\epsilon_i\}} \ln \left(1 - e^{(\mu-\epsilon_i)/kT} \right) \quad (5.10)$$

For fermions, the sum in (5.9) is just for $n_j = 0, 1$; and is hence trivial, and we find that, for fermions:

$$\ln \mathcal{Z}^{fermion} = \sum_{\{\epsilon_i\}} \ln \left(1 + e^{(\mu-\epsilon_i)/kT} \right) \quad (5.11)$$

In the classical limit

$$e^{(\mu-\epsilon)/kT} \ll 1$$

We have, using $\ln(1 + X) \approx X$, that both the boson and fermion grand partition functions are the same:

$$\ln \mathcal{Z}^{classical} \approx \sum_i e^{(\mu-\epsilon_i)/kT} = e^{\mu/kT} \sum_i e^{-\epsilon/kT}$$

i.e. $\mathcal{Z}^{classical} \approx \mathcal{Z}^{boson} \approx \mathcal{Z}^{fermion}$ in the classical limit.

Hence, in the classical limit, we can compute $S = -k \sum_i p_i \ln p_i$, where i is over the states of the gas. Below, j are the single particle energy levels:

$$\begin{aligned}
S &= -k \sum_i p_i \ln p_i \\
&= -k \sum_i \frac{e^{(\mu N_i - E_i)/kT}}{\mathcal{Z}} \ln \frac{e^{(\mu N_i - E_i)/kT}}{\mathcal{Z}} \\
&= -k \sum_i \frac{e^{(\mu N_i - E_i)/kT}}{\mathcal{Z}} \left(\ln e^{(\mu N_i - E_i)/kT} - \ln \mathcal{Z} \right) \\
&= -k \sum_i \frac{e^{(\mu N_i - E_i)/kT}}{\mathcal{Z}} \left(\frac{\mu N_i - E_i}{kT} - e^{\mu/kT} \sum_j e^{-\epsilon_j/kT} \right) \\
&= -k \left(\frac{\mu}{kT} \sum_i p_i N_i - \frac{1}{kT} \sum_i p_i E_i - e^{\mu/kT} \mathcal{Z} \right) \\
&= -k \left(\frac{\mu N}{kT} - \frac{U}{kT} - \mathcal{Z} e^{\mu/kT} \right)
\end{aligned}$$

Where we have used the partition function $\mathcal{Z} = \sum_j e^{-\epsilon_j/kT}$, and that the expressions for the average particle number and energy were written: $\sum_i N_i p_i = \langle N \rangle = N$ and $\sum_i E_i p_i = \langle E \rangle = U$.

Now, we have previously derived that $\mu = kT \ln \frac{n}{n_Q}$, and $\mathcal{Z} = n_Q V$. Hence, we have:

$$S = -k \left(N \ln \frac{n}{n_Q} - \frac{U}{kT} - \frac{n}{n_Q} n_Q V \right)$$

If we put:

$$U = \frac{3}{2} N k T \quad n V = N$$

Then:

$$S = N k \left(\frac{5}{2} + \ln \frac{n_Q}{n} \right) \tag{5.12}$$

Which is known as the *Sackur-Tetrode equation*.

Even though this calculation has been done in the classical limit, we have had to use the quantum physics of identical particles to get this expression correct. A classical result, built on quantum physics.

We can now easily compute the pressure and C_p . We start with pressure:

$$\begin{aligned}
 p &= T \left(\frac{\partial S}{\partial V} \right)_{N,U} \\
 &= NkT \frac{\partial}{\partial V} \left(\ln n_Q + \ln \frac{V}{N} \right)_{N,U} \\
 &= NkT \frac{\partial}{\partial V} \ln V \\
 &= \frac{NkT}{V} \\
 \Rightarrow pV &= NkT
 \end{aligned}$$

Where we have used that $n_Q(T)$ only, and that if we fix N and U , we therefore fix T . And finally, the heat capacity at constant pressure:

$$\begin{aligned}
 C_p &= T \left(\frac{\partial S}{\partial T} \right)_{p,N} \\
 &= NkT \left[\frac{\partial}{\partial T} \left(\ln \frac{NkT}{p} \right) + \frac{3}{2} \frac{1}{T} \right] \\
 &= \frac{5}{2} NkT
 \end{aligned}$$

Notice, we have also recovered a previously known result: $C_p - C_V = NkT$.

6 Fermi Gases

We shall focus on a non-interacting gas of spin- $\frac{1}{2}$ particles. At sufficiently low temperatures, quantum effects are crucial. So it remains to show when we can use the classical limit, and when quantum physics becomes important.

Examples of such systems are:

- Electrons in a metal ‘free electron theory’;
- ^3He atoms;
- Electrons in white dwarf stars;
- Neutrons in neutron stars;
- Nucleons in a nucleus.

Example We will show that free electrons in a metal at room temperature will be in the quantum regime, whereas hydrogen at STP will not.

We know we need to use quantum physics if $n \geq n_Q$.

Consider the electrons first:

If there is roughly 1 conduction electron per atom, in a metal of density $\rho \approx 10^3 \text{kgm}^{-3}$. So, we can compute the electron density:

$$n \approx \frac{10^3 \text{kgm}^{-3}}{10^{-25} \text{kg}} \approx 10^{28} \text{m}^{-3}$$

where we have used an approximate atomic mass.

Now,

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

So, we have quantum physics when:

$$\begin{aligned} n &\approx n_Q \\ \Rightarrow T &< n_Q^{2/3} \frac{2\pi\hbar^2}{mk} \\ \Rightarrow T &< 10^5 K \end{aligned}$$

Where we have used the mass of the electron. Notice, this upper temperature is well above room temperature, so free electrons in a metal are always acting according to quantum physics.

For hydrogen, we compute the number density via $pV = NkT$, and knowing that $n = \frac{N}{V}$. Thus:

$$\begin{aligned} n &\approx \frac{p}{kT} \\ &\approx \frac{10^5}{10^{-23} 10^2} \\ &= 10^{26} \text{m}^{-3} \\ \Rightarrow T &< \frac{10^{17} 10^{-67}}{10^{-27} 10^{-23}} K \\ &< 1K \end{aligned}$$

Where we have used the mass of a hydrogen atom. Notice that this temperature is very small, so quantum effects for hydrogen hardly ever come into play.

6.1 Ideal Fermi Gas at $T \approx 0$

Intuitively, expect the gas to be in its ground state at $T = 0$: all fermions occupy the lowest single particle states. So, up to some energy ϵ_F , we expect the system to be full, and above ϵ_F empty. All particles in the system occupy states below some fermi-energy.

$$\begin{aligned} \langle n(\epsilon) \rangle &= 1 \quad \epsilon < \epsilon_F \\ \langle n(\epsilon) \rangle &= 0 \quad \epsilon > \epsilon_F \end{aligned}$$

This is all using Fermi-Dirac statistics.

Notice that this is the case for $T = 0$. We get a step function. For $T > 0$, the step is smeared out slightly.

Now, we know

$$\langle n(\epsilon) \rangle = \frac{1}{e^{(\epsilon-\mu)/kT} + 1}$$

If $\epsilon > \mu$, then (under $T = 0$), we have that $\langle n \rangle = 0$.

Similarly, if $\epsilon < \mu$, then $\langle n \rangle = 1$.

Hence, we have the interpretation that the Fermi-energy ϵ_F is the value of the chemical potential μ at $T = 0$.

$$\epsilon_F \equiv \mu(T = 0) \quad (6.1)$$

At $T = 0$, all single particle states below ϵ_F are filled, whilst all those above are empty.

We denote a system at $T \approx 0$ as being a degenerate Fermi gas, and one at $T = 0$ an ideal Fermi gas.

So a gas of fermions that is cold enough so that nearly all states below ϵ_F are filled, and nearly all states above is called a degenerate fermi gas. This is just reiterating what has previously been said.

Now, if the gas is non-relativistic, we have the relations:

$$\begin{aligned} \epsilon_F &\equiv \frac{p_F^2}{2m} = \frac{\hbar^2 k_F^2}{2m} \\ k_B T_F &\equiv \epsilon_F \end{aligned}$$

Where we have thus defined the Fermi temperature T_F , Fermi momentum p_F , and Fermi wavenumber k_F in terms of the Fermi energy ϵ_F . Notice that we must distinguish between Boltzmann factor k_B and Fermi wavenumber k_F .

If the gas is ultra-relativistic ($m_0 \ll p$):

$$\begin{aligned} \epsilon_F &= cp_F \\ &= \hbar ck_F \end{aligned}$$

Clearly, ϵ_F must depend upon the number of particles N , so that we have that the number of particles below ϵ_F is N .

Example Compute ϵ_F for a 2D non-relativistic electron gas containing N electrons in an area A .

Let us construct a box, of side length L , so that $L^2 = A$. Then we have the Schrodinger equation, with its solution:

$$\begin{aligned} -\frac{\hbar^2}{2m} \nabla^2 \psi &= \epsilon \psi \\ \Rightarrow \psi &\propto \sin \frac{n_1 \pi x}{L} \sin \frac{n_2 \pi y}{L} \\ \epsilon &= \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + n_2^2) \end{aligned}$$

Where $n_1, n_2 > 0$ and are integers.

We must remember that for each state, we can have two spin-half electrons.

Hence, we want N to be twice the total number of single particle states with $\epsilon \leq \epsilon_F$:

$$n_1^2 + n_2^2 \leq \frac{\epsilon_F 2mL^2}{\hbar^2 \pi^2}$$

It is more convenient to work in terms of wavevectors $\mathbf{k} = (k_x, k_y)$, so that $\psi \propto \sin(k_x x) \sin(k_y y)$. We obviously have that $k_x \equiv \frac{n_1 \pi}{L}$ and $k_y \equiv \frac{n_2 \pi}{L}$. Hence, we can write the condition as:

$$\frac{\hbar^2 k^2}{2m} \leq \epsilon_F$$

Where $k^2 = k_x^2 + k_y^2$.

Notice that the distance between adjacent states in k -space is just $\frac{\pi}{L}$, and hence that the area occupied by one state is $(\frac{\pi}{L})^2$.

Now, we want to know how many states there are with $k_x^2 + k_y^2 \leq k_F^2$. That is, the area of the quarter-circle of radius k_F^2 , in k -space.

Thus, the number of electrons (which is twice the number of single particle energy states) in such an area is given by $N = 2 \times \text{area of quarter circle} / \text{area occupied by each state}$:

$$\begin{aligned} N &= 2 \frac{\frac{\pi k_F^2}{4}}{(\frac{\pi}{L})^2} \\ \Rightarrow k_F^2 &= \frac{N}{L^2} 2\pi \\ &= 2\pi n \end{aligned}$$

Where n is just the number density $n \equiv \frac{N}{L^2}$.

6.2 Density of States

Considering a 2D gas of Fermions:

Suppose we have an annulus, in the positive quarter of k -space. How many states reside here?

The number of states is obviously the area of the annulus, divided by the area of one state.

If the number of states is dn , and the annulus is $k \rightarrow dk$, then the area of the total circular annulus is $2\pi k dk$, and hence of the quarter annulus is $\frac{1}{4} 2\pi k dk$. We already have that the area taken up by one state is $(\frac{\pi}{L})^2$. Now, its important to note that we have been talking about the number of states. If we have a spin s -particle, there is allowed to be $2s + 1$ such particles in each state. We hence need to multiply any answer by the number of particles allowed in each state. For electrons, $s = \frac{1}{2}$, so everything is multiplied by 2. We hence can write:

$$\begin{aligned} dn &= 2 \frac{\frac{1}{4} 2\pi k dk}{(\frac{\pi}{L})^2} \\ &= \frac{k dk L^2}{\pi} \\ \Rightarrow \frac{dn}{dk} &= \frac{k L^2}{\pi} \end{aligned}$$

We hence have that $\frac{dn}{dk}$ is the density of states in k -space. The number of states dn per unit of k .

We can now rederive the Fermi-energy for our 2D electron gas.

The number of particles N below the Fermi-wavenumber k_F is the same as the total number of

particles in the system, at $T = 0$. We hence can say that the total number of particles is the (continuous) sum of the density of states, over all states up to the Fermi-state:

$$\begin{aligned}
 N &= \int_0^{k_F} dn \\
 &= \int_0^{k_F} \frac{dn}{dk} dk \\
 &= \int_0^{k_F} \frac{kL^2}{\pi} dk \\
 &= \frac{k_F^2 L^2}{2\pi} \\
 \Rightarrow k_F^2 &= \frac{N2\pi}{L^2}
 \end{aligned}$$

Hence, using the relation:

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m}$$

We can write ϵ_F :

$$\begin{aligned}
 \epsilon_F &= \frac{\hbar^2}{2m} \frac{2\pi N}{L^2} \\
 &= \frac{\pi \hbar^2}{m} \left(\frac{N}{L^2} \right) \\
 &= \frac{\pi \hbar^2 n}{m}
 \end{aligned}$$

Notice that the initial integral was for at $T = 0$. If $T \neq 0$, then we can write the much more general integral in terms of the mean number of particles:

$$N = \int_0^\infty \frac{dn}{dk} \langle n \rangle dk \quad (6.2)$$

If you recall we had the condition that $\langle n \rangle = 1$ for $k < k_F$, and zero elsewhere. This expression can be very hard to integrate, especially for bosons!

6.2.1 3D Density of States

We do an example to calculate the density of states for a 3D gas of *spinless* non-interacting particles, and use it to determine the chemical potential and energy of an ideal gas in the classical regime.

So, to begin, we know that the magnitude of the wavevector is given by $k^2 = k_x^2 + k_y^2 + k_z^2$, and that each state occupies a volume $\left(\frac{\pi}{L}\right)^3$.

We want to know how many states dn there are in the positive shell of $k \rightarrow k + dk$.

The volume of the entire shell is $4\pi k^2 dk$, and thus the volume of only the positive portion of the

shell is $\frac{1}{8}4\pi k^2 dk$. Hence, we can write:

$$\begin{aligned} dn &= \frac{\frac{1}{8}4\pi k^2 dk}{\left(\frac{\pi}{L}\right)^3} \\ &= \frac{L^3 k^2 dk}{2\pi^2} \\ \Rightarrow \frac{dn}{dk} &= \frac{k^2 L^3}{2\pi^2} \\ &= \frac{k^2 V}{2\pi^2} \end{aligned}$$

Thus, we have derived the density of states for a 3D gas of spinless fermions.

To get the chemical potential, we need to continue to solve N for μ , via:

$$N = \int_0^\infty \frac{dn}{dk} \langle n \rangle dk$$

Now, we have that

$$\langle n \rangle = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}$$

Which, in the classical limit (notice that the classical limit doesn't care if it's a boson or fermion) reduces to:

$$\langle n \rangle = e^{(\mu-\epsilon)/k_B T}$$

Hence:

$$N = \int_0^\infty \frac{V k^2}{2\pi^2} dk e^{-\epsilon/k_B T} e^{\mu/k_B T}$$

Notice, we also have that $\epsilon(k) = \frac{\hbar^2 k^2}{2m}$, so the integral is pretty hard to do. So, an alternative method, is to change variable, so right from the start, we have:

$$N = \int_0^\infty \frac{dn}{d\epsilon} \langle n \rangle d\epsilon$$

Hence, to do things using this method, we need the density of states in ϵ -space, as opposed to k -space. We can do this by chain rule:

$$\begin{aligned} \frac{dn}{d\epsilon} &= \frac{dn}{dk} \frac{dk}{d\epsilon} \\ &= \frac{k^2 V}{2\pi^2} \frac{1}{2} \sqrt{\frac{2m}{\epsilon \hbar^2}} \\ &= \frac{2m\epsilon}{\hbar^2} \frac{1}{2} \sqrt{\frac{2m}{\epsilon \hbar^2}} \\ &= \frac{V m^{3/2} \sqrt{2}}{2\pi^2 \hbar^3} \sqrt{\epsilon} \end{aligned}$$

Where we have made use of $\epsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow k = \sqrt{\frac{2m\epsilon}{\hbar^2}}$, and the original density of states $\frac{dn}{dk}$. We can immediately see that, for a non-relativistic gas:

$$\frac{dn}{d\epsilon} \propto \sqrt{\epsilon}$$

Thus, inserting this expression for $\frac{dn}{d\epsilon}$ back into the integral for N :

$$N = \frac{m^{3/2}\sqrt{2}V}{2\pi^2\hbar^3} \int_0^\infty \sqrt{\epsilon} e^{-\epsilon/k_B T} e^{\mu/k_B T} d\epsilon$$

Now, we start to try & simplify the integral.

Initially, we notice that we can do the following:

$$\begin{aligned} \int_0^\infty \sqrt{\epsilon} e^{-\epsilon/k_B T} d\epsilon &= (k_B T)^{3/2} \int_0^\infty \sqrt{\frac{\epsilon}{k_B T}} e^{-\epsilon/k_B T} d\left(\frac{\epsilon}{k_B T}\right) \\ &= (k_B T)^{3/2} \int_0^\infty \sqrt{X} e^{-X} dX \quad X \equiv \epsilon/k_B T \\ &= (k_B T)^{3/2} \frac{\sqrt{\pi}}{2} \end{aligned}$$

Where the actual integral has been looked up, and will be given.

Hence, we have:

$$\begin{aligned} N &= \frac{m^{3/2}\sqrt{2}V}{2\pi^2\hbar^3} (k_B T)^{3/2} \frac{\sqrt{\pi}}{2} e^{\mu/k_B T} \\ &= V \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} e^{\mu/k_B T} \\ &= V n_Q e^{\mu/k_B T} \\ \Rightarrow n = \frac{N}{V} &= n_Q e^{\mu/k_B T} \\ \Rightarrow \mu &= k_B T \ln \frac{n}{n_Q} \end{aligned}$$

Which is exactly the result we had before!

Obviously, we can write down an expression for the mean energy:

$$U = \int_0^\infty \frac{dn}{d\epsilon} \langle n \rangle \epsilon d\epsilon$$

Now, we have previously:

$$\frac{dn}{d\epsilon} = a\sqrt{\epsilon} \quad a \equiv \frac{Vm^{3/2}\sqrt{2}}{2\pi^2\hbar^3}$$

So:

$$\begin{aligned}
U &= a \int_0^\infty \sqrt{\epsilon} e^{(\mu-\epsilon)/k_B T} \epsilon d\epsilon \\
&= b \int_0^\infty \epsilon^{3/2} e^{-\epsilon/k_B T} d\epsilon \quad b \equiv a e^{\mu/k_B T} \\
&= b (k_B T)^{5/2} \int_0^\infty \left(\frac{\epsilon}{k_B T} \right)^{3/2} e^{-\epsilon/k_B T} d\left(\frac{\epsilon}{k_B T} \right) \\
&= b (k_B T)^{5/2} \int_0^\infty X^{3/2} e^{-X} dX \quad X \equiv \epsilon/k_B T \\
&= b (k_B T)^{5/2} \frac{3\sqrt{\pi}}{4} \\
&= \frac{V m^{3/2} \sqrt{2}}{2\pi^2 \hbar^3} e^{\mu/k_B T} (k_B T)^{5/2} \frac{3\sqrt{\pi}}{4} \\
&= \frac{V m^{3/2} \sqrt{2}}{2\pi^2 \hbar^3} (k_B T)^{5/2} \frac{3\sqrt{\pi}}{4} \frac{n}{n_Q} \\
&= \frac{V m^{3/2} \sqrt{2}}{2\pi^2 \hbar^3} (k_B T)^{5/2} \frac{3\sqrt{\pi}}{4} \frac{N}{V} \left(\frac{2\pi \hbar^2}{m k_B T} \right)^{3/2} \\
&= \frac{V m^{3/2} \sqrt{2} k_B^{5/2} T^{5/2} 3\sqrt{\pi} N 2^{3/2} \pi^{3/2} \hbar^3}{2\pi^2 \hbar^3 4 V m^{3/2} k_B^{3/2} T^{3/2}} \\
&= \frac{3}{2} N k_B T
\end{aligned}$$

Which again, is a result we previously knew.

In these two examples, we have used the 'standard integrals':

$$\begin{aligned}
\int_0^\infty x^{3/2} e^{-x} dx &= \frac{3}{4} \sqrt{\pi} \\
\int_0^\infty \sqrt{x} e^{-x} dx &= \frac{1}{2} \sqrt{\pi}
\end{aligned}$$

Which will be given, if needed.

We can use these couple of examples as a prototype for finding the average value of something: add up the average number of particles in a particular state, times the density of particles in a particular state, multiply by the thing you want the average of. This gives the average of the quantity over the whole system.

So, the average number of particles is given by:

$$\langle N \rangle = N = \int_0^\infty \frac{dn}{dk} \langle n \rangle dk \quad (6.3)$$

And the average internal energy of the system:

$$\langle U \rangle = U = \int_0^\infty \frac{dn}{dk} \langle n \rangle \epsilon dk \quad (6.4)$$

In the expression for U , it is required to know if the gas is non-relativistic, relativistic or ultra-relativistic. For non- and ultra-relativistic, we have the expressions:

$$\epsilon^{non} = \frac{\hbar^2 k^2}{2m} \quad \epsilon^{ultra} = \hbar ck$$

Suppose we want the average velocity of a single particle. We compute this by finding the average velocity of all particles, and divide by the number of particles:

$$\langle v \rangle = \frac{1}{N} \int_0^\infty \frac{dn}{dk} \langle n \rangle v dk \quad (6.5)$$

To get an expression for v , we note that kinetic energy is both equal to $\frac{\hbar^2 k^2}{2m}$ and to $\frac{1}{2}mv^2$. Hence, $v = \frac{\hbar k}{m}$. Note that this is only for non-relativistic.

If we want to find the variance on a quantity, N , say, we merely need to compute:

$$\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 \quad (6.6)$$

Back to Fermi gases:

Let's calculate the Fermi-energy of a 3D electron gas.

We have the definition that $\epsilon_F \equiv \mu(T=0)$. So, the mean number of particles is simply given by:

$$N = \int_0^{k_F} \frac{dn}{dk} dk$$

Where we will use the previously derived $\frac{dn}{dk} = \frac{Vk^2}{2\pi^2}$ for spinless particles. We must use a spin multiplicity factor of 2; and we have also used the fact that particles either reside under the Fermi-energy, or not at all: the step-function. Thus:

$$N = \int_0^{k_F} \frac{2Vk^2}{2\pi^2} dk = \frac{Vk_F^3}{3\pi^2}$$

Hence, we use $n = \frac{N}{V}$, to see that:

$$k_F = (3\pi^2 n)^{1/3} \quad (6.7)$$

Which obviously holds for non- or relativistic systems.

Now, for non-relativistic, we have that:

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m}$$

Hence, we can write the Fermi-energy in terms of number density n :

$$\epsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \quad (6.8)$$

Now, we shall suppose (and subsequently prove) that if $T < T_F$ (remembering that $k_B T_F \equiv \epsilon_F$), then quantum effects are important. Hence, we have the classical regime if:

$$k_B T \gg \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$$

Or, that:

$$n \ll \left(\frac{2mk_B T}{\hbar^2} \right)^{3/2} \frac{1}{3\pi^2} \quad (6.9)$$

Now, we have that the quantum concentration n_Q is given by:

$$n_Q = \left(\frac{2mk_B T}{2\pi\hbar^2} \right)^{3/2}$$

Hence, we see that (6.9) is equivalent to:

$$n \ll n_Q \frac{8}{3\sqrt{\pi}}$$

Hence, we have that $n \ll n_Q$ for classical. Which is our previous definiton, but derived by stating that $T \gg T_F$ for classical.

Now, let's calculate the internal energy of a non-relativistic 3D gas of electrons. We have straight away that:

$$U = \int_0^{k_F} \frac{V k^2}{\pi^2} \frac{\hbar^2 k^2}{2m} dk = \frac{V}{\pi^2} \frac{\hbar^2}{2m} \frac{k_F^2}{5}$$

Now, from (6.7), we have:

$$k_F = (3\pi^2 n)^{1/3} \Rightarrow N = \frac{V k_F^3}{3\pi^2}$$

Hence,

$$U = \frac{3}{5} N \frac{\hbar^2 k_F^2}{2m}$$

But we also have the relation that $\epsilon_F = \frac{\hbar^2 k_F^2}{2m}$. Hence:

$$U = \frac{3}{5} N \epsilon_F \quad (6.10)$$

Now, if we want to calculate the pressure p , we initially start by writing:

$$dU = TdS - pdV$$

Which, at $T = 0$, reduces to:

$$p = - \left(\frac{\partial U}{\partial V} \right)_N$$

Hence:

$$\begin{aligned} p &= - \frac{\partial}{\partial V} \left(\frac{3}{5} N \epsilon_F \right) \\ &= - \frac{3}{5} N \frac{\partial \epsilon_F}{\partial V} \end{aligned}$$

Where we can do the differentiation:

$$\frac{\partial \epsilon_F}{\partial V} = - \frac{2}{3} \frac{\epsilon_F}{V}$$

Hence:

$$p = \frac{2}{5} \frac{N\epsilon_F}{V} = \frac{2}{5} n\epsilon_F$$

Which we can rearrange into the equation of state for a Fermi-gas at low temperature:

$$pV = \frac{2}{5} N\epsilon_F \quad (6.11)$$

This is the equivalent of $pV = Nk_B T$.

To get C_V , we take:

$$C_V = \left. \frac{\partial U}{\partial T} \right)_V = 0$$

At $T = 0$, as U is independent of T at 0. This is a little useless, as it does not tell us what happens as $T \rightarrow 0$. To find out this behavior, we need to do some small T corrections to U . To do this properly, we need to evaluate the integral:

$$U = \int_0^\infty \frac{dn}{dk} \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1} \epsilon dk$$

Which is hard.

We can estimate the correction by saying that only particles within $k_B T$ of ϵ_F move. So, the number of excited particles is:

$$\frac{k_B T}{\epsilon_F} N$$

So, additional energy is of the order:

$$\frac{k_B T}{\epsilon_F} N k_B T$$

Hence, U needs to be corrected by this factor:

$$U = \frac{3}{5} N\epsilon_F + \alpha \frac{(k_B T)^2}{\epsilon_F} N$$

Where α is some constant. If this correction is done exactly, one finds that $\alpha = \frac{\pi^2}{4}$. Hence, if we now calculate C_V using this corrected version of U , we find:

$$C_V = \left. \frac{\partial U}{\partial T} \right)_V = \frac{N k_B^2 T \pi^2}{2\epsilon_F}$$

6.2.2 Low T Corrections to N, U

Now, we have that:

$$\begin{aligned} N &= \int_0^\infty \frac{dn}{d\epsilon} \langle n \rangle d\epsilon \\ &= \int_0^\infty \frac{dn}{d\epsilon} \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1} d\epsilon \\ U &= \int_0^\infty \frac{dn}{d\epsilon} \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1} \epsilon d\epsilon \end{aligned}$$

We have previously derived that:

$$\frac{dn}{d\epsilon} = \frac{3}{2} N \epsilon_F^{-3/2} \epsilon^{1/2}$$

So, to solve these integrals, we have objects of the form:

$$I = \int_0^\infty \frac{f(\epsilon)}{e^{(\epsilon-\mu)/k_B T}} d\epsilon$$

Now, we must be able to write the answer in terms of:

$$I = \int_0^\mu f(\epsilon) d\epsilon + \text{corrections in } T \rightarrow 0$$

So, we want to try to get our integral in that form.

Suppose we define:

$$z \equiv \frac{\epsilon - \mu}{k_B T}$$

Hence, we see that $z(\epsilon = 0) = -\mu/k_B T$, and $\epsilon = k_B T z + \mu$. I will now omit the subscript B from Boltzmanns constant. Hence, we have:

$$I = kT \int_{-\mu/kT}^\infty \frac{f(zkT + \mu)}{e^z + 1} dz$$

Which we can split into 2 integrals:

$$I = kT \int_{-\mu/kT}^0 \frac{f(zkT + \mu)}{e^z + 1} dz + kT \int_0^\infty \frac{f(zkT + \mu)}{e^z + 1} dz$$

And we can invert the firsts limits:

$$I = kT \int_0^{\mu/kT} \frac{f(\mu - zkT)}{e^{-z} + 1} dz + kT \int_0^\infty \frac{f(zkT + \mu)}{e^z + 1} dz$$

Now, if we write:

$$\frac{1}{e^{-z} + 1} = 1 - \frac{1}{e^z + 1}$$

Then the integral becomes:

$$\begin{aligned} I &= kT \int_0^\infty \frac{f(zkT + \mu)}{e^z + 1} dz + kT \left(\int_0^{\mu/kT} f(\mu - zkT) dz - \int_0^{\mu/kT} \frac{f(\mu - zkT)}{e^z + 1} dz \right) \\ &= kT \int_0^\mu f(\epsilon) d\epsilon - kT \left(\int_0^{\mu/kT} \frac{f(\mu - zkT)}{e^z + 1} dz - \int_0^\infty \frac{f(zkT + \mu)}{e^z + 1} dz \right) \end{aligned}$$

Now, in the limit of $T \rightarrow 0$, $z \rightarrow \infty$. Hence, the middle integral above can be written to have an upper limit of ∞ :

$$I = \int_0^\mu f(\epsilon) d\epsilon + kT \int_0^\infty \frac{f(\mu + zkT) - f(\mu - zkT)}{e^z + 1} dz$$

The second integral can be Taylor expanded to:

$$I_2 = 2(kT)^2 \frac{df(\mu)}{d\mu} \int_0^\infty \frac{z}{e^z + 1} dz$$

Where we can look up the integral as being:

$$\int_0^{\infty} \frac{z}{e^z + 1} dz = \frac{\pi^2}{12}$$

Thus:

$$I = \int_0^{\mu} f(\epsilon) d\epsilon + \pi^2 \frac{(kT)^2}{6} \frac{df(\mu)}{d\mu}$$

Now, applying this result to N :

$$N = \frac{3}{2} N \epsilon_F^{-3/2} \int_0^{\infty} \frac{\epsilon^{1/2}}{e^{(\epsilon-\mu)/kT} + 1} d\epsilon$$

We hence see that $f(\epsilon) = \epsilon^{1/2}$ and $f(\mu) = \mu^{1/2}$. We hence have, for the integral I_N :

$$I_N = \frac{2}{3} \mu^{3/2} + \frac{(kT\pi)^2}{6} \frac{1}{2} \mu^{-1/2}$$

Thus:

$$\begin{aligned} N &= \frac{3}{2} N \epsilon_F^{-3/2} \left(\frac{2}{3} \mu^{3/2} + \frac{(kT\pi)^2}{6} \frac{1}{2} \mu^{-1/2} \right) \\ &= N \left(\frac{\mu}{\epsilon_F} \right)^{3/2} \left(1 + \frac{(kT\pi)^2}{8} \mu^{-2} \right) \\ \Rightarrow 1 &= \frac{\mu}{\epsilon_F} \left(1 + \frac{(kT\pi)^2}{8} \mu^{-2} \right)^{2/3} \\ \Rightarrow \mu &= \epsilon_F \left(1 + \frac{(kT\pi)^2}{8} \mu^{-2} \right)^{-2/3} \\ &= \epsilon_F \left(1 - \left(\frac{kT}{\epsilon_F} \right)^2 \frac{\pi^2}{12} \right) \end{aligned}$$

Where the last step has been done by a binomial expansion, and noting that $\mu(0) = \epsilon_F$.

Now, doing so similarly for U , we find:

$$\begin{aligned} U &= \frac{3}{2} N \epsilon_F^{-3/2} I_U \\ I_U &= \int_0^{\infty} \frac{\epsilon^{3/2}}{e^{(\epsilon-\mu)/kT} + 1} d\epsilon \\ &= \frac{2}{5} \mu^{5/2} + \frac{(kT\pi)^2}{6} \frac{3}{2} \mu^{1/2} \\ \Rightarrow U &= \frac{3}{5} N \epsilon_F \left(1 + \frac{5}{12} \pi^2 \left(\frac{kT}{\epsilon_F} \right)^2 \right) \end{aligned}$$

Which gives the previously stated correction factor. The last step has been done by substituting in the derived expression for μ .

6.3 Example: Electrons in Metals

Now, if $T < T_F$, we need to model electrons as behaving quantum mechanically.

For metals, we have data which show that $T_F \approx 10^4 \rightarrow 10^5 \text{K}$, and $v_F \approx 1\%c$. Hence, metals at room temperature behave via non-relativistic quantum mechanics.

If we suppose that the conduction electrons in a metal form a gas of free electrons, then it will be a non-relativistic degenerate fermi gas at room temperature. That is, occupancies of states below the Fermi-energy is = 1. Now, electrons are actually (weakly) bound to the ionic lattice core, where the binding will have the effect of dragging on the motion of electrons, and to thus increase the mass of the electron, This effect will be ignored, but will be noted upon when we compare to data.

We have computed that quantum theory predicts:

$$C_{electrons}^{quantum} = \frac{\pi^2}{2} N k_B \left(\frac{k_B T}{\epsilon_F} \right)$$

Where we have ignored any contributions to C due to the ionic core. So, what would classical theory predict? We have already done this, to the Einstein solid. It is just $\frac{1}{2} k_B N$ per degree of freedom. Thus:

$$C_{electrons}^{class} = \frac{3}{2} N k_B$$

Now, if we include the contribution from the lattice $3Nk_B$, where we have supposed 6 degrees of freedom (!):

$$C_{total}^{class} = 3Nk_B + \frac{3}{2} N k_B = \frac{9}{2} N k_B$$

Now, experiment yields $C \approx 3Nk_B$; which appears to be in agreement with the classical prediction where there are no electrons.

We can explain this discrepancy, by noting that $C_{electrons}^{quantum}$ is small for $T < T_F$. That is, if $\frac{k_B T}{\epsilon_F} \ll 1$. Putting typical numbers in, we find that the quantum correction of the classical result is of the order 1%. This would not show up on a crude experiment, but does in a more accurate experiment.

Heat capacities at low T have been accurately measured to go like:

$$C \approx aT + bT^3$$

Where bT^3 is due to ionic contributions, and aT from electron contributions.

Experimental data results in a value for a :

$$a = 2.08 \times 10^{-3} \text{Jmol}^{-1} \text{K}^{-2}$$

We get a value, from potassium data:

$$a = \frac{\pi^2}{2} N k_B \left(\frac{k_B}{\epsilon_F} \right) = 1.7 \times 10^{-3} \text{Jmol}^{-1} \text{K}^{-2}$$

So, our value is 20% off. This is however, our prediction with no ionic corrections. Our result should always be smaller than experiment, as ionic cores ‘drag’ electrons back, effectively increasing their mass.

$$a \propto \frac{1}{\epsilon_F} \propto m$$

Thus, if m were 20% bigger when ionic interactions taken into account, then the agreement would be perfect.

6.4 Example: Liquid ^3He

^3He is a fermion.

Compute the Fermi-energy and find the temperature below which quantum effects are important. i.e. compute ϵ_F and T_F . Given that the density is $\rho = 81 \text{ kgm}^{-3}$.

Hence, we compute the number density n :

$$n = \frac{N}{V} = \frac{81}{3 \times 1.67 \times 10^{-27}} = 1.6 \times 10^{28} \text{ m}^{-3}$$

Where we have divided the density by the 3 times the mass of the proton. Hence, we have:

$$\begin{aligned} \epsilon_F &= \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} = 4.2 \times 10^{-4} \text{ eV} \\ T_F &= \frac{\epsilon_F}{k_B} = 5 \text{ K} \\ v_F &= \sqrt{\frac{2\epsilon_F}{m}} = 160 \text{ m s}^{-1} \end{aligned}$$

Where we have also compute the Fermi-velocity, to check that it is non-relativistic (which is blatantly is!).

So, for $T < 5 \text{ K}$, we expect:

$$C_V = \frac{\pi^2}{2} N k_B \left(\frac{k_B T}{\epsilon_F} \right) = (1.0 \text{ K}^{-1}) N k_B T$$

And again, experiment yields 2.8 K^{-1} , which is higher than our prediction.

Hence, interactions between ^3He is obviously not negligible.

Especially at $T < 2 \text{ mK}$, where we have a discontinuity in the heat capacity at the transition into a superfluid, where the ^3He atoms pair up into bosonic pairs.

6.5 Example: Electrons in Stars

We start by asking: Do the electrons in the Sun form a degenerate fermi gas?

So, given that the core temperature is $T \approx 10^7\text{K}$, we need to be able to compare it with the fermi temperature, which we need to calculate.

Note, if $T = 10^7\text{K}$, then the thermal energy $\epsilon = k_B T \approx 10^7 \times 10^{-23} \approx 10^3\text{eV}$. Now, this is a lot higher than the binding energy ($= 13.6\text{eV}$), hence there will not be much atomic hydrogen - it will be mostly ionised. Now, we can compute T_F via:

$$T_F = \frac{k_B}{\epsilon_F} = \frac{1}{k_B} \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$$

Where we have assumed non-relativistic.

We can work out n via the mass of the Sun. If we assume that the Sun is only made up of protons and electrons.

$$n = \frac{N}{V} = \frac{M_\odot}{M_p + M_e} \frac{1}{V_\odot} = \frac{M_\odot}{M_p} \frac{1}{V_\odot}$$

Where we have used the fact that $M_e \ll M_p$. We have also assumed one electron per proton. Using $M_\odot \approx 2 \times 10^{30}\text{kg}$ and $R_\odot \approx 7 \times 10^8\text{m}$, we have:

$$n \approx 10^{30}\text{m}^{-3}$$

From which we can calculate:

$$T_F \approx 10^5\text{K}$$

Which is two orders of magnitude less than the core temperature, therefore, $T > T_F$, therefore electrons in the Sun do not form a degenerate fermi gas.

6.5.1 White Dwarf Stars

Stellar evolution starts with hydrogen gas collapsing under gravity to the point where pp fusion can occur at $T \approx 10^7\text{K}$. The stars radius is stabilised by the outward radiation pressure from the gas of ions, electrons and photons. The electrons are not (necessarily) degenerate. The outward radiation pressure is stabilised (or stabilises) the inward gravitational attraction due to mass.

When the proton fuel runs out, the radiation pressure falls, and the star collapses under gravity until the core becomes hot enough for the He to ignite at $T \approx 10^8\text{K}$.

The process continues until no more nuclear fuel is left to burn. However, such stars are kept from further collapse by the presence of an outward pressure due to the degenerate electron gas. These types of stars are called ‘white dwarfs’.

Now, given the mass of a white dwarf, we ought to be able to compute its radius.

Consider a shell at radius r , thickness dr . Now, the inward force due to gravity is balanced by the outward force due to degenerate electrons. We can compute the inward gravitational force:

$$dF = 4\pi r^2 dr \rho(r) \frac{GM(r)}{r^2}$$

Where $M(r)$ is the mass of the star inside a sphere of radius r . Notice that the volume of the shell is $4\pi r^2 dr$, hence its mass is just $4\pi r^2 dr \rho(r)$.

An outward force would come from a difference in pressure between the inner and outer surfaces of the shell, which would be of the form:

$$\begin{aligned} -dF &= [p(r+dr) - p(r)]4\pi r^2 \\ &= dp4\pi r^2 \end{aligned}$$

Which we can substitute in for:

$$-dp4\pi r^2 = 4\pi r^2 dr \rho(r) \frac{GM(r)}{r^2} \quad (6.12)$$

$$\Rightarrow -\frac{dp}{dr} = \rho(r) \frac{GM(r)}{r^2} \quad (6.13)$$

$$\Rightarrow -\int_{p(0)}^{p(R)} dp = \int_0^R \rho(r) \frac{GM(r)}{r^2} dr \quad (6.14)$$

Now, to do this integrals properly requires a numerical approximation. So we use various approximations.

We assume that $p(0) \gg p(R)$, thus helping with the integral on the LHS. We shall also assume that any integral for the density $\rho(r)$ over r results in some ‘average density’ $\tilde{\rho}$. Now, we have that the mass inside some sphere can be given by:

$$M(r) = \int_0^r 4\pi r'^2 \rho(r') dr' = \tilde{\rho} \frac{4\pi r^3}{3}$$

Where we have used our approximation of average density. Thus, (6.14) becomes:

$$\begin{aligned} p(0) &= \int_0^R \rho(r) \frac{GM(r)}{r^2} dr \\ &= 4\pi G \tilde{\rho}^2 \int_0^R \frac{1}{r^2} \frac{r^3}{3} dr \\ &= \frac{4\pi G \tilde{\rho}^2 R^2}{6} \\ &\equiv p \end{aligned}$$

If we do the simple substitution that:

$$\tilde{\rho} = \frac{M}{V} = \frac{M}{\frac{4}{3}\pi R^3}$$

Then we have an expression for the inward pressure due to gravity:

$$p = 4\pi G \frac{R^2}{6} \left(\frac{M}{\frac{4}{3}\pi R^3} \right)^2 \propto \frac{M^2}{R^4}$$

Now, we have previously computed the pressure exerted by degenerate fermions:

$$p = \frac{2}{5} n \epsilon_F = \frac{2}{5} n^{5/3} \frac{\hbar^2}{2m} (3\pi^2)^{2/3}$$

Where we can compute n as we did for the Sun. We assume the core to be composed of helium, which is 1 electron per proton. We use u to denote the atomic mass unit:

$$n = \frac{M}{\frac{4}{3}\pi R^3} \frac{1}{2u}$$

Therefore, we have that the pressure due to the degenerate electrons is like:

$$p \propto \frac{M^{5/3}}{R^5}$$

Thus, equating these two pressures (due to degeneracy and gravity) we obtain:

$$\begin{aligned} R &= \alpha M^{-1/3} \\ \alpha &\equiv \frac{\hbar^2}{2m} 3^{2/3} \pi^{4/3} \left(\frac{3}{8\pi n} \right)^{5/3} \frac{8\pi}{3G} \\ &= 4 \times 10^{16} \text{mkg}^{1/3} \end{aligned}$$

Data obtains $\alpha = 7 \times 10^{16} \text{mkg}^{1/3}$, which is a pretty good agreement! The agreement becomes absolute if the density integral is done properly.

Hence, we see that such a star is stable, and degeneracy pressure ‘always’ wins. The reason for quotation marks, is that if the mass is above a certain limit, electron degeneracy pressure cannot sustain the equilibrium, and the star collapses further, into a neutron degenerate state.

We should check that the white dwarfs in the table are made of a degenerate core of electrons, and are not-relativistic.

We know that the temperature of the star $T \approx 10^7 \text{K}$. So, we need to compute T_F :

$$k_B T_F = \epsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$$

To compute n , we do an order of magnitude calculation that is VERY rough:

$$n = \frac{M}{u} \frac{1}{\frac{4}{3}\pi r^3} \approx \frac{10^{30}}{10^{-27} 10^{20}} \approx 10^{35} \text{m}^{-3}$$

Hence, we find that $T_F \approx 10^9 \text{K} > T$. Hence, electrons degenerate.

How fast are the electrons? We proceed via:

$$\epsilon_F = \frac{1}{2} m v_F^2 = k_B T$$

Hence, we have:

$$v_F = \sqrt{\frac{2k_B T}{m}} = 10^7 \text{ms}^{-1}$$

Which is a lot less than c , hence non-relativistic.

What happens for more massive stars? We note that the electrons will become ultra-relativistic, and so we move from being able to use $\epsilon = \frac{\hbar^2 k^2}{2m}$ to having to use:

$$\epsilon = \hbar c k$$

Hence, we recalculate the density of states:

$$\begin{aligned}
 dn &= \frac{4\pi k^2 dk}{8} \frac{1}{\left(\frac{\pi}{L}\right)^2} \\
 \Rightarrow \frac{dn}{dk} &= \frac{Vk^2}{\pi^2} \\
 \Rightarrow \frac{dn}{d\epsilon} &= \frac{dn}{dk} \frac{dk}{d\epsilon} = \frac{Vk^2}{\pi^2} \frac{1}{\hbar c} \\
 &= \frac{V\epsilon^2}{(\hbar c)^3 \pi^2}
 \end{aligned}$$

Where we now have the density of states in energy-space. Notice that the density of states for an ultra-relativistic gas of fermions is now proportional to ϵ^2 , whereas the density of states for non-relativistic fermions was $\propto \sqrt{\epsilon}$.

At $T = 0$, we can write that:

$$p - \left. \frac{\partial U}{\partial V} \right)_N$$

So, we compute the internal energy U via:

$$U = \int_0^{\epsilon_F} \epsilon \frac{dn}{d\epsilon} d\epsilon = \frac{V\epsilon_F^4}{(\hbar c)^3 \pi^2 4}$$

And, to differentiate this properly, we need to figure out $\epsilon_F(V)$. We do this via:

$$\begin{aligned}
 N &= \int_0^{\epsilon_F} \frac{dn}{d\epsilon} d\epsilon \\
 &= \frac{V\epsilon_F^3}{(\hbar c)^3 \pi^2 3} \\
 \Rightarrow \epsilon_F(V) &= (3\pi^2)^{1/3} \hbar c \left(\frac{N}{V} \right)^{1/3} \\
 \Rightarrow U &= \frac{V}{(\hbar c)^3 \pi^2 4} (3\pi^2)^{4/3} (\hbar c)^4 \left(\frac{N}{V} \right)^{4/3}
 \end{aligned}$$

Hence, we have pressure as being just:

$$p - \left. \frac{\partial U}{\partial V} \right)_N = \frac{1}{3} \frac{U}{V}$$

One-third of the energy-density of the system. Hence looking at everything, we have that:

$$p \propto \frac{N^{4/3}}{V^{4/3}}$$

And we see that $N \propto M$ and $V \propto R^3$. Thus:

$$p \propto \frac{M^{4/3}}{R^4}$$

For a gas of ultra-relativistic fermions.

Now, this dependence for the degeneracy pressure is such that there exists a maximum mass for which the pressures due to gravity and degeneracy balance. That is, there exists a maximum mass for which degeneracy pressure can sustain collapse due to gravity. This maximum mass is $1.4M_{\odot}$: the Chandrasekhar Mass.

As the star collapses ϵ_F rises. Eventually, particle physics becomes important and we get inverse beta-decay $pe^- \rightarrow n\nu_e$ and all protons and electrons disappear leaving only neutrons; where the neutrinos will fly out. There will then be a neutron degeneracy pressure which supports against further collapse (until its critical mass of $1.8M_{\odot}$ is reached).

7 Bose Gases

We are interested in low T behaviour. As $T \rightarrow 0$ we expect even classically that particles will occupy only the lowest energy level. So, how low must T be for macroscopic occupation of the ground state? That is, the majority of particles in the ground state.

So, if we write down expressions for the two lowest possible energy states of a system:

$$\epsilon_0 = \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 (1^2 + 1^2 + 1^2) \quad \epsilon_1 = \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 (2^2 + 1^2 + 1^2)$$

Thus, the spacing between these levels is:

$$\epsilon_1 - \epsilon_0 = \frac{3\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2$$

For the ground state to contain most of the particles, we want:

$$k_B T \leq \epsilon_1 - \epsilon_0$$

If $L = 1\text{cm}$, $m = 6.6 \times 10^{-27}\text{kg}$, then:

$$T \leq \frac{10^{-68}10}{10^{-26}1^{-4}} = 10^{-14}\text{K}$$

Which is very low! This however, has been calculated using classical arguments, and the result is very different if we use a quantum mechanical description of identical particles.

Recall:

$$\langle n(\epsilon) \rangle_{BE} = \frac{1}{e^{(\epsilon-\mu)/k_B T} - 1}$$

Initially notice, when $e^{(\epsilon-\mu)/k_B T} = 1$ then the above becomes singular. We shall use the initial approximation for the total number of particles:

$$N \approx \int_0^{\infty} \frac{dn}{d\epsilon} \frac{1}{e^{(\epsilon-\mu)/k_B T} - 1} d\epsilon$$

It will become clear as to why this is only an approximation. One thing to note is that the density of states is proportional to $\sqrt{\epsilon}$, and hence the result of this integral at the lowest single particle energy state $\epsilon_0 = 0$ is zero. The exact form is actually purely a summation:

$$N = \sum_i \langle n(\epsilon_i) \rangle$$

So, we start to analyse the distribution function:

If N is fixed, then as T falls, μ must therefore rise. If we have that $\epsilon \geq 0$, and if we take the minimum energy level to be ϵ_0 , then we have $\mu \leq \epsilon_0$ so that there are no negative-particle-number occupancies (equivalent to saying there is always the requirement of $\epsilon - \mu > 0$) of any energy levels. We can set $\epsilon_0 = 0$, hence we have that $\mu \leq 0$.

Now, we see that there is a potential ‘problem’. μ cannot increase beyond $\epsilon_0 = 0$ at some critical temperature T_c . Hence, we have that $\mu = 0$ at $T = T_c$. Thus, we can say (and this isn’t an approximation):

$$N \equiv \int_0^\infty \frac{dn}{d\epsilon} \frac{1}{e^{\epsilon/k_B T_c} - 1} d\epsilon$$

So, we have the interpretation that $T = T_c$ is the lowest temperature in which $\langle n \rangle_{BE}$ works. We say this because for $T < T_c$, we have that $\mu > 0$, which is impossible.

So, let’s compute $\langle n \rangle_{BE}$ for the lowest energy state $\epsilon_0 = 0$:

$$\frac{1}{e^{-\mu/k_B T} - 1} = \frac{1}{1 - \frac{\mu}{k_B T} - 1} = -\frac{k_B T}{\mu} \equiv N_0$$

Where we have used the Taylor expansion $e^x = 1 + x + x^2 + \dots$. Hence, we have that N_0 is the number of particles in the ground state. Notice that $N_0 \rightarrow \infty$ as $\mu \rightarrow 0$. Now, we also know that $N_0 \leq N$. Hence $-\frac{k_B T}{\mu} \leq N$; thus

$$\mu \geq -\frac{k_B T}{N}$$

Hence, as we have that $\mu \leq 0$ and the above ‘lower’ restraint, we have narrowed down the position of μ very finely. For a system of 10^{23} particles, μ is very very close to zero, but not quite. In actual fact, the splitting between μ and ϵ_0 is a lot less than that between ϵ_0 and ϵ_1 .

We now have a new particle distribution function for $T < T_c$:

$$\langle n \rangle = \frac{1}{e^{\epsilon/k_B T} - 1}$$

Where we now have solved the problem of having $\mu > 0$.

So, to summarise thus far, we have shown that as $T \rightarrow 0$, the occupancy of the ground state, N_0 , tends to infinity. We also have that as $T \rightarrow 0$, $\mu \rightarrow 0$ very quickly for a macroscopic system.

So, we can now write down a correct expression for the number of particles in the system: we take out of the summation just the term due to the ground state:

$$N = N_0 + \int_0^\infty \frac{dn}{d\epsilon} \frac{1}{e^{\epsilon/k_B T} - 1} d\epsilon$$

That we have not changed the lower limit of the integral is not a problem: the integral is zero for $\epsilon = 0$ anyway. Notice, we have also put $\mu = 0$, as the energy level splitting is massive compared to $\mu - \epsilon_0$. Now, we can do this integral, after inserting in the expression for the density of states in energy-space (for non-relativistic bosons). So, how does N_0 vary for $T < T_c$, where we assume $\mu = 0$? So, writing the integral:

$$N = N_0 + \int_0^\infty \frac{Vm^{3/2}}{\sqrt{2\pi^2\hbar^3}} \frac{\epsilon^{1/2} d\epsilon}{e^{\epsilon/k_B T} - 1} \quad (7.1)$$

Now, we previously wrote that:

$$\begin{aligned} N &\equiv \int_0^\infty \frac{dn}{d\epsilon} \frac{1}{e^{\epsilon/k_B T_c} - 1} d\epsilon \\ &= \frac{Vm^{3/2}}{\sqrt{2\pi^2\hbar^3}} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\epsilon/k_B T} - 1} \\ &= \frac{Vm^{3/2}}{\sqrt{2\pi^2\hbar^3}} (k_B T_c)^{3/2} \int_0^\infty \frac{(\epsilon/k_B T_c)^{1/2} d(\epsilon/k_B T_c)}{e^{\epsilon/k_B T} - 1} \\ &= \frac{Vm^{3/2}}{\sqrt{2\pi^2\hbar^3}} (k_B T_c)^{3/2} \int_0^\infty \frac{X^{1/2} dX}{e^X - 1} \end{aligned}$$

Infact, the integral can be looked up, to give:

$$\int_0^\infty \frac{X^{1/2} dX}{e^X - 1} = 2.315$$

Thus, (7.1) can be written:

$$\int_0^\infty \frac{dn}{d\epsilon} \frac{1}{e^{\epsilon/k_B T_c} - 1} d\epsilon = N_0 + \int_0^\infty \frac{dn}{d\epsilon} \frac{1}{e^{\epsilon/k_B T} - 1} d\epsilon$$

Now, we notice a similarity between all factors in both integrals, except for T and T_c , which we can factor out:

$$T_c^{3/2} \alpha = N_0 + T^{3/2} \alpha \quad (7.2)$$

Where:

$$\begin{aligned} \alpha &\equiv \frac{Vm^{3/2}}{\sqrt{2\pi^2\hbar^3}} (k_B)^{3/2} \int_0^\infty \frac{X^{1/2} dX}{e^X - 1} \\ &= \frac{N}{T_c^{3/2}} \end{aligned}$$

Therefore, inserting this into (7.2) gives a relation for how the number of particles in the ground state varies as T gets close to T_c :

$$N_0 = N \left[1 - \left(\frac{T}{T_c} \right)^{3/2} \right]$$

We are also able to write down the condensation temperature:

$$T_c = \left(\frac{\sqrt{2}\pi^2 \hbar^3 \frac{N}{V}}{m^{2/3} \times 2.315} \right)^{2/3} \frac{1}{k_B}$$

Thus, this is the temperature at which Bose-Einstein condensation (BEC) takes place. Putting various numbers in:

$$T_c = 3.31 \frac{\hbar^2}{mk_B} n^{2/3}$$

Now, if we just write down the inequality for which we get BEC:

$$\begin{aligned} T &< T_c \\ \Rightarrow T &< \frac{\hbar^2}{mk_B} n^{2/3} \\ \Rightarrow \left(\frac{mk_B T}{\hbar^2} \right)^{3/2} &< n \\ \Rightarrow n_Q &< n \end{aligned}$$

Where we have recognised the definition of the quantum density.

So, for $T < T_c$, it is not only the region where BEC takes place, but it is also the region where quantum effects become important. So, as soon as we get quantum effects (in an ideal Bose gas), all particles jump into the ground state.

For ${}^4\text{He}$, with $\rho = 145 \text{ kg m}^{-3}$ we have $T_c = 3\text{K}$; which is a lot greater than from the previous classical argument! n is computed from ρ , via:

$$n = \frac{N}{V} = \frac{\rho}{n_n \times m_n} = \frac{145}{4 \times 1.67 \times 10^{-27}} = 2.17 \times 10^{28} \text{ m}^{-3}$$

Where n_n is the number of nucleons ($2p + 2n$) each having a mass m_n . Thus, T_c is finally computed by using this, and that m is the mass of a helium-4 atom $= 4m_n = 4u$, where u is the atomic mass unit.

Experimentally, BEC has been observed in many systems; but for the first time in 1995, using a gas of Rubidium atoms.

7.1 Black Body Radiation

Consider a gas of photons in thermal equilibrium. So, the gas is ideal (except in ‘early universe’ phase), ultra-relativistic (obviously) and $\mu = 0$.

To see why $\mu = 0$, we note that $dS = 0$ in equilibrium. Therefore, so is:

$$\left(\frac{\partial S}{\partial N} \right)_{U,V} dN = 0$$

Now, we have that a gas of photons cannot have a fixed number of particles (hence $dN \neq 0$), as, for example, atoms are constantly radiating them. Hence, we see that:

$$\left(\frac{\partial S}{\partial N} \right)_{U,V} = 0$$

However, we have the definition:

$$\mu \equiv -T \left(\frac{\partial S}{\partial N} \right)_{U,V}$$

Therefore, we see that $\mu = 0$. Hence, we have:

$$\langle n(\epsilon) \rangle = \frac{1}{e^{\epsilon/k_B T} - 1}$$

Lets compute the energy density $\frac{U}{V}$ of a gas of photons:

$$\frac{U}{V} = \frac{1}{V} \int_0^\infty \frac{dn}{d\epsilon} \langle n(\epsilon) \rangle \epsilon d\epsilon$$

Using the ultra-relativistic form for the density of states in energy-space (previously derived) and using a ‘spin multiplicity’ factor of 2, as there can be two polarisation states ‘in one’, we have:

$$\begin{aligned} \frac{U}{V} &= \frac{1}{V} \int_0^\infty \frac{V}{\pi^2} \left(\frac{\epsilon}{\hbar c} \right)^2 \frac{1}{\hbar c} \frac{\epsilon}{e^{\epsilon/k_B T} - 1} d\epsilon \\ &= \frac{1}{(\hbar c)^3 \pi^2} \int_0^\infty \frac{\epsilon^3}{e^{\epsilon/k_B T} - 1} d\epsilon \\ &= \frac{(k_B T)^4}{(\hbar c)^3 \pi^2} \int_0^\infty \frac{(\epsilon/k_B T)^3}{e^{\epsilon/k_B T} - 1} d(\epsilon/k_B T) \\ &= \frac{(k_B T)^4}{(\hbar c)^3 \pi^2} \int_0^\infty \frac{X^3}{e^X - 1} dX \\ &= \frac{(k_B T)^4}{(\hbar c)^3 \pi^2} \frac{\pi^4}{15} \\ \Rightarrow \frac{U}{V} &= \frac{\pi^2}{15(\hbar c)^3} (k_B T)^4 \end{aligned}$$

Now, to proceed, we shall discuss a little bit about blackbody radiation:

Suppose we have a box of photons in thermal equilibrium (whose energy-density we have just computed). The box is completely isolated, except for a very small hole. Photons are able to leave this hole, being in thermal equilibrium with the other photons still inside the box, hence blackbody radiation. Any photons incident upon the hole, from outside, will be able to enter the hole, hence a blackbody absorber. If all photons inside the box move towards the side with the hole (of area A), then the volume of photons being ejected per second is just cA . However, not all photons will be moving in that direction, so we must integrate over the solid angle, to give $\frac{1}{4}cA$.

So, we ask the question, what is the power being radiated by the hole? This is just the total energy ejected per second:

$$P = \frac{1}{4} c A \frac{U}{V}$$

Hence, inserting our expression for the energy density:

$$P = \left(\frac{\pi^2}{60 \hbar^3 c^2} k_B^4 \right) T^4 \equiv \sigma T^4$$

Where we have arrived at Stefan’s law, with his constant:

$$\sigma \equiv 5.67 \times 10^{-8} W m^{-2} s^{-1} K^{-4}$$

Now, how is this power distributed over wavelengths? This will lead us to the Planck distribution, and being able to predict the CMB.

Aside: CMB. The Cosmic Microwave Background arose in the very early universe. When the temperature of the universe was so high that protons and electrons could not combine to form hydrogen, or any other elements, the ambient photons were being constantly scattered by this hot-plasma. As the universe cooled, Hydrogen formed, and photons stopped being scattered by the protons and electrons. They had, however, been in thermal equilibrium with them. So, at the time of recombination (where hydrogen formed), the photons suddenly had nothing to scatter off, so they maintained their temperature/energy from when they were in thermal equilibrium. We are able to measure this background radiation.

The CMB is a perfect blackbody radiation distribution, at a temperature of $\approx 2.7\text{K}$. On a finer resolution however (order mK), we find anisotropies in the otherwise perfect blackbody spectrum. These anisotropies give information about how the very first matter was formed, in its density. Initial density fluctuations from recombination have left their mark in the form of the CMB anisotropies, and from this, we can find information about the early universe.

7.2 Spectral Energy Density

Now, let's calculate how the energy density $\frac{U}{V}$ is distributed over wavelengths λ . That is, the spectral energy density.

Now, we have that:

$$u(\lambda)d\lambda$$

Is the energy per unit volume, in the wavelength interval $\lambda \rightarrow \lambda + d\lambda$. Now, we previously calculated the total energy density:

$$\frac{U}{V} = \frac{1}{\pi^2(\hbar c)^3} \int_0^\infty \frac{\epsilon^3}{e^{\epsilon/k_B T} - 1} d\epsilon \quad (7.3)$$

This is obviously the same as integrating $u(\lambda)d\lambda$ over all λ . Hence:

$$\frac{U}{V} = \int_0^\infty u(\lambda)d\lambda \quad (7.4)$$

$$= \frac{1}{\pi^2(\hbar c)^3} \int_0^\infty \frac{\epsilon^3}{e^{\epsilon/k_B T} - 1} d\epsilon \quad (7.5)$$

That is to say:

$$u(\lambda)d\lambda = 2 \frac{dn}{d\epsilon} \epsilon \langle n \rangle \frac{1}{V} d\epsilon$$

Where the factor 2 comes from there being 2 polarisation states.

Now, we can find $u(\lambda)$ by changing variables. We have that $\epsilon = \hbar\omega = \frac{hc}{\lambda}$. Thus:

$$d\epsilon = -\frac{hc}{\lambda^2} d\lambda$$

Thus, inserting these expressions into (7.3) results in:

$$\frac{U}{V} = \int_0^\infty \frac{\left(\frac{hc}{\lambda}\right)^3}{e^{hc/\lambda k_B T} - 1} \frac{1}{\pi^2(\hbar c)^3} \frac{hc}{\lambda^2} d\lambda$$

Where the minus sign has been absorbed into the integrand, by symmetry arguments. If this is now compared with (7.4), we find (after cleaning up the above):

$$u(\lambda) = \frac{(2\pi)^3 hc}{\pi^2 \lambda^5} \frac{1}{e^{hc/\lambda k_B T} - 1}$$

Thus, we have derived what the energy density of a particular wavelength is: $u(\lambda)$. This is known as the Planck Formula. If we let $\lambda \rightarrow \infty$, then we can Taylor expand the exponential, and we will end up with the classical Rayleigh-Jeans limit:

$$u(\lambda) = 8\pi \frac{hc}{\lambda^5} \frac{\lambda k_B T}{hc} = \frac{8\pi k_B T}{\lambda^4}$$

Notice, for this formula now (which is purely classical) there is a huge problem, and it is predicted that $u(\lambda = 0) = \infty$. So, an infinite distribution for zero wavelength. This is, of course ridiculous, and is known as the UV-catastrophe.

We can find the wavelength which has maximum power associated with it. That is, a turning point of the $u(\lambda)$ curve. This is:

$$\frac{du}{d\lambda} = 0$$

This is known as Wein's displacement law. However, to actually differentiate $u(\lambda)$ gets tedious, so we apply a 'trick'. Let:

$$u \equiv \frac{f(x)}{\lambda^5} \quad x \equiv \lambda T$$

Hence, if we write:

$$\begin{aligned} \frac{du}{d\lambda} &= \frac{d}{d\lambda} \left(\frac{f(x)}{\lambda^5} \right) \\ &= \frac{1}{\lambda^5} \frac{df}{d\lambda} + f(x) \frac{d}{d\lambda} \frac{1}{\lambda^5} \\ &= \frac{1}{\lambda^5} \frac{df}{dx} \frac{dx}{d\lambda} - f(x) \frac{5}{\lambda^6} \\ &= \frac{1}{\lambda^5} \frac{df}{dx} T - f(x) \frac{5}{\lambda^6} \\ &= 0 \\ \Rightarrow \frac{1}{\lambda^5} \frac{df}{dx} T &= f(x) \frac{5}{\lambda^6} \\ \Rightarrow x \frac{df}{dx} &= 5f(x) \end{aligned}$$

Hence, the solution to this equation is that $x = \text{constant}$, or $T\lambda = \text{constant}$.

Therefore, we have derived that the wavelength which has maximum power ascribed to it, at a particular temperature, can be found from $T\lambda = \text{constant}$. Thus, for two temperatures T_1, T_2 ; their maximum powers are at wavelengths λ_1, λ_2 . If $T_1 < T_2$, then $\lambda_1 > \lambda_2$.

Sometimes we want $u(\omega)d\omega$, which is the spectral distribution in terms of angular frequency. We have that $\epsilon = \hbar\omega$; and thus:

$$u(\omega)d\omega = 2 \frac{dn}{d\omega} d\omega \langle n(\omega) \rangle \frac{\hbar\omega}{V}$$

So, it remains to calculate the density of states in ω -space:

$$\frac{dn}{d\omega} = \frac{dn}{dk} \frac{dk}{d\omega}$$

Using the relation $\omega = ck$, we can then write:

$$\begin{aligned} \frac{dn}{d\omega} &= \frac{dn}{dk} \frac{1}{c} \\ &= \frac{Vk^2}{2\pi^2} \frac{1}{c} \\ &= \frac{V\omega^2}{2c^2\pi^2} \\ &= \frac{V\omega^2}{2c^3\pi^2} \end{aligned}$$

Therefore, putting everything in:

$$u(\omega)d\omega = 2 \frac{V\omega^2}{2c^3\pi^2} d\omega \frac{1}{e^{\hbar\omega/k_B T} - 1} \frac{\hbar\omega}{V}$$

Cleaning up:

$$u(\omega)d\omega = \frac{\hbar\omega^3}{c^3\pi^2(e^{\hbar\omega/k_B T} - 1)} d\omega$$

Now, let us leave that alone.

7.2.1 Pressure of a Photon Gas

Let us now calculate the pressure due to a bose (photon) gas, in thermal equilibrium. To do so, we calculate S , and differentiate it to get p . Recall that we have previously derived:

$$S = -k_B \sum_{states} \frac{e^{(\mu N_s - E_s)/k_B T}}{\mathcal{Z}} \left(\frac{\mu N_s - E_s}{k_B T} - \ln \mathcal{Z} \right)$$

Where the sum is over all single particle energy states. We have also derived:

$$\ln \mathcal{Z} = - \sum_i \ln \left(1 - e^{(\mu - \epsilon_i)/k_B T} \right)$$

Now, we have that $\mu = 0$. We hence see that the expression for S simplifies somewhat:

$$S = -k_B \sum_{states} \frac{e^{-E_s/k_B T}}{\mathcal{Z}} \left(\frac{-E_s}{k_B T} - \ln \mathcal{Z} \right)$$

Notice that the first term is the same as writing $\sum_i p_i E_i$, which is just U . The second term is just:

$$k_B \ln \mathcal{Z} \sum_i p_i = k_B \ln \mathcal{Z}$$

The expression for $\ln \mathcal{Z}$ can be made continuous via:

$$\ln \mathcal{Z} = - \int_0^\infty d\epsilon \frac{dn}{d\epsilon} \ln(1 - e^{-\epsilon/k_B T})$$

Which we evaluate:

$$\begin{aligned} \ln \mathcal{Z} &= - \frac{V}{\pi^2} \frac{1}{(\hbar c)^2} \int_0^\infty \epsilon^2 \ln(1 - e^{-\epsilon/k_B T}) d\epsilon \\ &= - \frac{V}{\pi^2} \frac{1}{(\hbar c)^3} (k_B T)^3 \int_0^\infty \left(\frac{\epsilon}{k_B T} \right)^2 \ln(1 - e^{-\epsilon/k_B T}) d \left(\frac{\epsilon}{k_B T} \right) \\ &= - \frac{V}{\pi^2} \frac{1}{(\hbar c)^3} (k_B T)^3 \int_0^\infty X^2 \ln(1 - e^{-X}) dX \end{aligned}$$

The integral is evaluated to give:

$$\int_0^\infty X^2 \ln(1 - e^{-X}) dX = - \frac{1}{3} \frac{\pi^4}{15}$$

Therefore, we see that:

$$\begin{aligned} S &= -k_B \sum_{states} \frac{e^{-E_s/k_B T}}{\mathcal{Z}} \left(\frac{-E_s}{k_B T} - \ln \mathcal{Z} \right) \\ &= \frac{k_B U}{k_B T} + k_B \ln \mathcal{Z} \\ &= \frac{U}{T} + V \left(\frac{k_B T}{\hbar c} \right)^3 \frac{\pi^2 k_B}{45} \end{aligned}$$

Now, we have previously derived that:

$$\frac{U}{V} = \frac{\pi^2 k_B^4 T^4}{15(\hbar c)^3}$$

Hence, inserting things, and clearing up, results in:

$$S = \frac{U}{T} + \frac{1}{3} \frac{U}{T} = \frac{4}{3} \frac{U}{T}$$

Now the, pressure is found from:

$$p = T \left(\frac{\partial S}{\partial V} \right)_U$$

Now, to do this properly, we need to be careful; and find $S(U, V)$. Now, we just worked out (putting all constants together):

$$U = aVT^4$$

Thus, we see that $S = \frac{4}{3}aVT^3$. Therefore:

$$\begin{aligned}
 S &= \frac{4}{3}aV \left(\frac{U}{aV} \right)^{3/4} \\
 &= \frac{4}{3}a \left(\frac{U}{a} \right)^{3/4} V^{1/4} \\
 \Rightarrow \left(\frac{\partial S}{\partial V} \right)_U &= \frac{1}{3}a \left(\frac{U}{a} \right)^{3/4} V^{-3/4} \\
 &= \frac{1}{3}a \left(\frac{U}{aV} \right)^{3/4} \\
 &= \frac{1}{3}aT^3 \\
 \Rightarrow p &= T \left(\frac{\partial S}{\partial V} \right)_U \\
 &= \frac{1}{3}aT^4 \\
 &= \frac{1}{3} \frac{U}{V}
 \end{aligned}$$

Hence, we have that the pressure exerted by a gas of photons is one third of the energy-density of the photons. Which is, incidentally, an identical result as found for the pressure due to ultra-relativistic electrons (fermions)

Now, for adiabatic expansions, we have that $dS = 0$. Classically, this corresponded with the result of $PV^\gamma = \text{const}$. However, here, if we look at the expression for S , and put it equal to a constant, we have:

$$VT^3 = \text{const}$$

For a photon gas.

8 Lattice Vibrations of a Solid

We've thus far been discussing a gas of photons by specifying the occupancies of each energy level. Thus, systems previously were determined by the set $\{n_i\}$; where n_i was the number of photons in energy level ϵ_i . Thus, we were able to compute the average internal energy of the system via:

$$U = \sum_i \langle n \rangle_i \epsilon_i \approx \int_0^\infty \frac{dn}{d\omega} \langle n \rangle \epsilon d\omega$$

We use this framework as an exact analogy to lattice vibrations of a solid:

Photons in energy level $\epsilon_i = \hbar\omega_i$ can be viewed as quanta associated with a set of quantum harmonic oscillators. That is, we model a solid as being a set of harmonic oscillators, each loaded with some quanta. The analogy goes that the set of harmonic oscillators is the same as the set of energy levels of a photon gas. In quantising the lattice vibrations, we introduce the term 'phonon' as the analogy to 'photon' for a photon gas. A phonon is the quanta of lattice vibrations. A phonon is the sound

‘particle’, where a photon was a light ‘particle’.

For a cube of some solid, with N atoms on some periodic lattice, there will be $3N$ normal modes. This is the total number of frequencies the system is allowed to vibrate in; such is the definition of a normal mode.

So, we have that we have n_i phonons in energy level ϵ_i . Hence, we have an energy $n_i \hbar \omega_i$ on oscillator i . As we had no need (or idea) about a fixed number of photons in a system, we also have that the number of phonons in a system is not fixed; thus, $\mu = 0$ for lattice vibrations. We also use Bose-Einstein statistics.

In Einstein’s model of a solid that we discussed at the start of the course, it was assumed that all $3N$ oscillate with the same frequency; thus $\epsilon_1 = \epsilon_2 = \dots = \epsilon_{3N}$. So, for an Einstein solid:

$$\begin{aligned} U^E &= \sum_{i=1}^{3N} \langle n_i \rangle_{BE} \epsilon_i \\ &= \sum_{i=1}^{3N} \frac{1}{e^{\hbar\omega/k_B T} - 1} \hbar\omega_i \\ &= \frac{3N \hbar\omega}{e^{\hbar\omega/k_B T} - 1} \end{aligned}$$

Which is a result that previously took us a lot longer to derive, as we previously had to physically count all states available. From this, we can just take the differential w.r.t. T to find the heat capacity.

Now, Debye realised that the $3N$ modes do not oscillate with a single frequency - as Einstein had assumed. But rather, the allowed frequencies are those of harmonic waves in a box. Thus, we have a wavenumber $k_i = \frac{n_i \pi}{L}$. Thus, we are able to write down a density of states. We use the relation $k = \frac{\omega}{u}$, where u is the speed of wave propagation, which is the speed of phonons, which is the speed of sound. Thus:

$$\begin{aligned} \frac{dn}{d\omega} &= \frac{dn}{dk} \frac{dk}{d\omega} \\ &= \frac{V k^2}{2\pi^2} \frac{1}{u} \\ &= \frac{V \omega^2}{2\pi^2 u^3} \end{aligned}$$

Now, the multiplicity factor we use is ‘3’. This comes from the consideration that we are able to excite 2 transverse and 1 longitudinal sound waves in a $3d$ cube. Thus, the useable density of states is thus:

$$\frac{dn}{d\omega} = 3 \frac{V \omega^2}{2\pi^2 u^3}$$

So now, lets calculate the average energy of a Debye solid:

$$U^D = \int_0^{\omega_D} \frac{dn}{d\omega} \langle n \rangle \epsilon d\omega$$

Now, notice: for a photon gas, the upper limit was infinity. That was because there was an (essentially) infinite range of frequencies open to the system. We cannot assume this for lattice vibrations. So, we assume that only $\omega < \omega_D$, that is $\lambda > \lambda_D$. So, lets try to compute this cut-off.

Suppose atoms are spaced by an amount d . Then, the shortest possible wavelength that is able to be fully supported by atoms are $\lambda_D \approx 2d$. If we try to stick more than one wave between atoms, then nothing is excited, as there are no atoms there, hence pointless. Therefore, we are able to estimate the shortest wavelength that will be excited. The atomic spacing d is of the order $\frac{1}{n^{1/3}}$, the inverse of the cube-root of the number-density. We see that ω is of the order $\frac{u}{\lambda}$ (up to 2π). Hence:

$$\omega_D \approx u \left(\frac{N}{V} \right)^{1/3}$$

We can calculate this exactly, by noting that there should be exactly $3N$ energy levels. So:

$$\begin{aligned} 3N &= \int_0^\infty \frac{dn}{d\omega} d\omega \\ &= \frac{3V}{2\pi^2 u^3} \frac{\omega_D^3}{3} \\ \Rightarrow \omega_D &= u \left(6\pi^2 \frac{N}{V} \right)^{1/3} \end{aligned}$$

Therefore, we have an expression for the Debye cut-off frequency ω_D . Notice, its in good agreement with previous estimation. So, going back to the calculation of the internal energy of a Debye solid, inserting expressions for the density of states and BE distribution:

$$U^D = \frac{3V\hbar}{2\pi^2 u^3} \int_0^\infty \frac{\omega^3 d\omega}{e^{\hbar\omega/k_B T} - 1}$$

This integral is hard to do, and we are unable to express it in the dimensionless terms we have used for bose gases. So, lets compute the heat capacity directly:

$$\begin{aligned} C^D &= \frac{\partial U}{\partial T} \\ &= \frac{3V\hbar}{2\pi^2 u^3} \int_0^{\omega_D} \frac{\omega^3 e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} \frac{\hbar\omega}{k_B T^2} d\omega \end{aligned}$$

Now, put:

$$x \equiv \frac{\hbar\omega}{k_B T}$$

Then:

$$C^D = \frac{3V\hbar}{2\pi^2 u^3} \frac{(k_B T)^4}{\hbar} \frac{1}{T} \int_0^{x_D} \frac{x^4}{(e^x - 1)^2} dx$$

This can be cleaned up, after a lot of work, to:

$$C^D = 3Nk_B \left(\frac{3}{x_D^3} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \right)$$

Let us now look at the high and low temperature limits:

For high T , we see that x is small. Hence, the exponential in the bottom is expanded to $e^x = 1 + x$; and the exponential in the top just to unity. Thus, the integral itself is:

$$\int_0^{x_D} \frac{x^4}{(x + 1 - 1)^2} dx = \int_0^{x_D} \frac{x^4}{x^2} dx = \frac{1}{3} x_D^3$$

Hence, we see:

$$C^D \approx 3Nk_B \frac{3}{x_D^3} \frac{x_D^3}{3} = 3Nk_B$$

Therefore, the high temperature behaviour of the heat capacity is a constant: $C^D = 3Nk_B$.

In low temperatures, we see that $x \rightarrow \infty$. Hence, the upper limit of the integral goes to infinity. We see that the $\frac{e^x}{(e^x - 1)^2}$ term goes to e^{-x} , for large x . Therefore, the integral just becomes:

$$\int_0^\infty x^4 e^{-x} dx$$

Which is just a number, β , say. Then:

$$C^D \approx 3Nk_B \frac{3}{x_D^3} \beta \propto T^3$$

Hence, we see that the low temperature heat capacity goes as T^3 . We find that experimental data

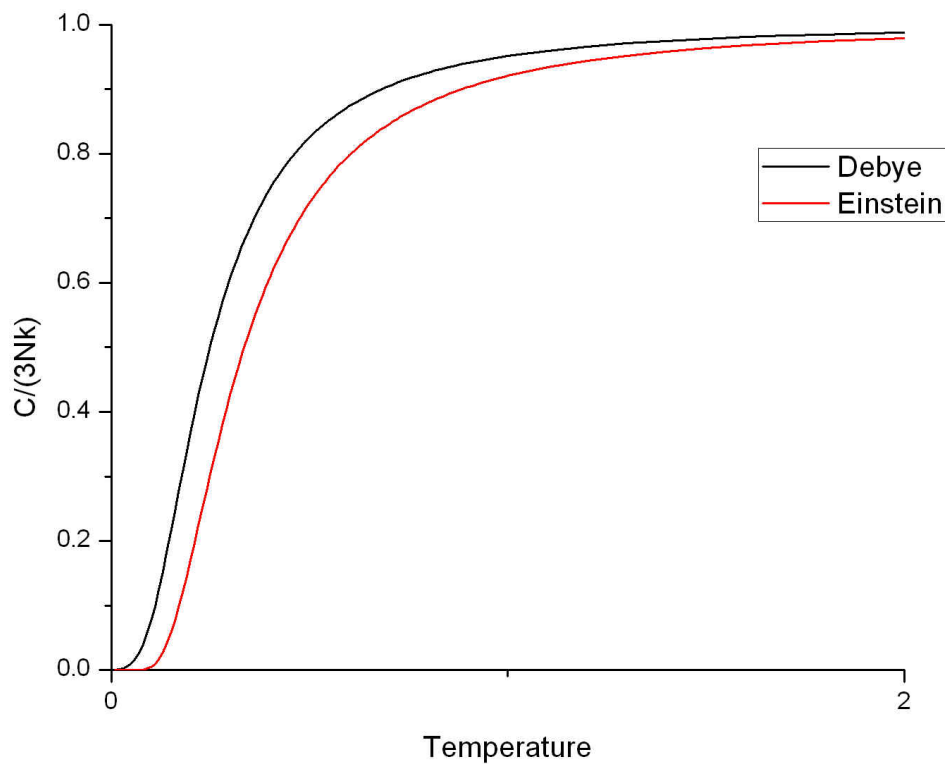


Figure 2: Heat capacity predictions of Debye and Einstein, Data will sit on Debye's curve, as opposed to Einstein's.

sits on the Debye curve, as opposed to that predicted with Einstein's approximation.

A Colloquial Summary

This is a summary, based on the summary lecture.

The fundamental assumption pretty much everything is based upon is that for a closed system in equilibrium, all microstates are equally likely. Now, if a particular macrostate has more microstates than others, then it is more likely to be ‘picked’.

There may be more than one way (microstate) of finding the system with a particular number of particles, energy, volume. These macroscopic quantities (N, U, V) then define a macrostate.

A unique equilibrium macrostate usually exists. It is the macrostate with the overwhelmingly most microstates. Now, we define entropy via $S = -k_B \ln g$. Where g is the number of microstates in a given macrostate. So, in equilibrium, S is a maximum. Thus, $dS = 0$. Therefore, for some macroscopic variable X , $\frac{\partial S}{\partial X} = 0$. This is a consequence of the chain rule. These variables are then used to define temperature, chemical potential and pressure:

$$\frac{\partial S}{\partial N} \propto \mu \quad \frac{\partial S}{\partial U} \propto T \quad \frac{\partial S}{\partial V} \propto p$$

Now, let's consider an ‘open system’; one that can transfer particles and energy with a reservoir. We do this by considering our system of interest as being part of a bigger system. Suppose our system of interest has particle number and energy N_s, U_s . Then, we have derived that the probability to find the system in such a state; in a single quantum state (microstate) is:

$$P(N_s, U_s) = \frac{e^{\frac{N_s \mu - U_s}{k_B T}}}{\mathcal{Z}}$$

Which is the Gibbs distribution.

From now, we shall consider our systems to be composed of non-interacting particles. We consider fermions and bosons. We can derive that the mean number of particles in a given quantum state is:

$$\langle n \rangle_{FD} = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1}$$
$$\langle n \rangle_{BE} = \frac{1}{e^{(\epsilon - \mu)/k_B T} - 1}$$

These tell us what the average number of particles in a particular energy state is.

We have the classical limit where $\langle n \rangle_{FD} \approx \langle n \rangle_{BE} \approx e^{\frac{\mu - \epsilon}{k_B T}}$. The classical limit can be interpreted as being where the box defined by the de Broglie wavelength of the particles is very much less than the distance between the particles. Or, $n \ll n_Q$, where $n_Q \approx \frac{1}{\lambda_Q^3}$.

We write some general formulae for finding the particle number N , internal energy U of the system and entropy S :

$$N = \int_0^\infty \frac{dn}{dk} \langle n \rangle dk$$
$$U = \int_0^\infty \frac{dn}{dk} \langle n \rangle \epsilon dk$$
$$S = -k_B \sum p_i \ln p_i$$

The integral for N can be done, and then solved for the chemical potential μ . We must specify whether to use non-relativistic or ultra-relativistic expressions $\epsilon = \frac{\hbar^2 k^2}{2m}$ or $\epsilon = \hbar ck$. We now consider fermions and boson separately.

Fermions Fermions have anti-symmetric wavefunctions, which has the consequence of excluding there ever being more than one fermion in a single particle energy state.

We have considered examples of electrons in metals and white dwarf stars.

We can use an approximation of $T = 0$ to rewrite the particle distribution function. We say that the occupancy of all (almost) single particle states below some $\epsilon = \epsilon_F$ is total, and that (almost) no particles have energies above ϵ_F . Hence, the integral for the number of particles N has upper limit k_F , and $\langle n \rangle = 1$ in this range. From this, we are able to derive an equation for ϵ_F, k_F and use $\epsilon_F = k_B T_F$ to find the fermi-temperature.

For $T \neq 0$, we imagine the step function crumbling over, to give the actual distribution. We use this idea in calculating low temperature corrections to U . We say that the particles within $k_B T$ of ϵ_F move up in energy by amount $k_B T$. This allows us to write:

$$\Delta U = \frac{k_B T}{\epsilon_F} N k_B T$$

That the internal energy is now dependent upon T gives the experimentally verified result of linear heat capacity. Note, at $T = 0$, U is independant of T , and $C = 0$.

Bosons Bosons have symmetric wavefunctions, and hence have no restriction on the number in any single particle energy state.

We see that if N is fixed, then, as T falls, μ rises. We see that $\mu < 0$; however, if T keeps decreasing, μ will go above zero (where zero is defined as being the same as the lowest energy state). When this happens, there is a negative particle occupancy. So, to get around this, we say that below some critical temperature, T_c , $\mu = 0$. We say that T_c is the minimum temperature for which we can ignore the ground state occupation. We also find that the ground state is macroscopically occupied by particles. Infact, we define:

$$N \equiv \int_0^\infty \frac{dn}{d\epsilon} \frac{1}{e^{\epsilon/k_B T_c} - 1} d\epsilon$$

Now, for $T < T_c$, we are able to say that $N = N_0 + N_e$, where N_0 is the number in the ground state and N_e is the number of particles in excited state, where:

$$N_e = \int_0^\infty \frac{dn}{d\epsilon} \frac{1}{e^{\epsilon/k_B T} - 1} d\epsilon$$

Using these two integrals, we are able to calculate the number of particle in the ground state. We are also able to calculate T_c .

If we have a gas of photons in thermal equilibrium, we cannot expect the particle number to stay constant; however, we still say that $\mu = 0$, from considerations of the entropy in equilibrium. This modifies the BE distribution, to give us that for a gas of photons. We are easily able to compute the energy density of such a gas, and hence the power outputted per unit area, and can thus derive Stefan's law $P = \sigma T^4$. The distribution of this power over wavelengths (spectral distribution) can

thus be calculated. We write $u(\lambda)d\lambda$ as being the energy per unit volume in a wavelength interval. We can write the same thing in ω :

$$u(\omega)d\omega = \frac{1}{V} \int \frac{dn}{d\omega} \langle n \rangle \epsilon d\omega$$

Where we write $\epsilon = \hbar\omega$ and the particle distribution is the modified BE distribution with $\mu = 0$. Now, we actually have that:

$$\frac{U}{V} = \int u(\omega)d\omega$$

As energy density. We are able to calculate the pressure exerted by a photon gas as being $\frac{1}{3} \frac{U}{V}$, which is the same as that due to ultra-relativistic electrons.

B Calculating the Density of States

The number of states dn , of spinless particles in a small 3D annulus, in k -space is given by the volume of the annulus (which is $\frac{1}{8}$ of the volume of the whole annulus) divided by the volume taken up by one state. Thus:

$$\begin{aligned} dn &= \frac{\frac{1}{8}4\pi k^2 dk}{\left(\frac{\pi}{L}\right)^3} \\ &= \frac{Vk^2}{2\pi^2} dk \end{aligned}$$

We have used that $L^3 = V$. Hence, rearranging, we have the density of states, in k -space, of spinless particles:

$$\frac{dn}{dk} = \frac{Vk^2}{2\pi^2} \tag{B.1}$$

This will be our starting point for all subsequent calculations. To get the density of states in energy-space, we require a relationship between the wavenumber k and energy ϵ , and hence we must specify whether or not the gas is non-relativistic, or ultra-relativistic (massless).

If the particles are fermions, and carry an intrinsic spin s , then this is modified to:

$$\frac{dn}{dk} = (2s + 1) \frac{Vk^2}{2\pi^2}$$

If the particles are photons, they carry a spin of 1. However, we actually use a factor of 2, as there are two polarisation states of a photon associated with each ‘state’. Hence, for photons:

$$\frac{dn}{dk} = \frac{Vk^2}{\pi^2}$$

Proceeding with all subsequent calculations assume spinless.

B.1 Energy Space: Non-Relativistic

Suppose we want the density of states in energy space, that is:

$$\frac{dn}{d\epsilon}$$

We use the chain rule of differentiation to write:

$$\frac{dn}{d\epsilon} = \frac{dn}{dk} \frac{dk}{d\epsilon}$$

The link between wavenumber k and energy ϵ , for non-relativistic particles is:

$$\epsilon = \frac{\hbar^2 k^2}{2m} \tag{B.2}$$

Hence, rearranging:

$$k = \left(\frac{2m}{\hbar^2} \right)^{1/2} \sqrt{\epsilon}$$

Therefore:

$$\frac{dk}{d\epsilon} = \left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{1}{2\sqrt{\epsilon}}$$

Now, we must also put $\frac{dn}{dk}$ in terms of ϵ , which must be done using the non-relativistic expression above in (B.2):

$$\frac{dn}{dk} = \frac{V k^2}{2\pi^2} = \frac{V}{2\pi^2} \frac{2m\epsilon}{\hbar^2}$$

Therefore, putting this all together:

$$\begin{aligned} \frac{dn}{d\epsilon} &= \frac{dn}{dk} \frac{dk}{d\epsilon} \\ &= \frac{V}{2\pi^2} \frac{2m\epsilon}{\hbar^2} \left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{1}{2\sqrt{\epsilon}} \\ &= \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon} \end{aligned}$$

So, the density of states, in energy-space, of a gas of non-relativistic particles is thus:

$$\frac{dn}{d\epsilon} = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon} \quad (\text{B.3})$$

B.2 Energy Space: Ultra-Relativistic

If the gas is ultra-relativistic, we must use the following relation $\epsilon = pc$, hence:

$$\epsilon = \hbar ck \quad (\text{B.4})$$

Thus, we have the chain-rule expression:

$$\frac{dn}{d\epsilon} = \frac{dn}{dk} \frac{dk}{d\epsilon}$$

Where we now see that:

$$\frac{dk}{d\epsilon} = \frac{1}{\hbar c}$$

We also have that:

$$\frac{dn}{dk} = \frac{V k^2}{2\pi^2} = \frac{V \epsilon^2}{2\pi^2 (\hbar c)^2}$$

Therefore, the density of states for an ultra-relativistic gas of spinless particles is:

$$\frac{dn}{d\epsilon} = \frac{V \epsilon^2}{2\pi^2 (\hbar c)^3} \quad (\text{B.5})$$

C Deriving FD & BE Distributions

The Gibbs probability distribution:

$$P(N, U) = \frac{e^{\beta(\mu N - U)}}{\mathcal{Z}}$$

Where $\beta \equiv \frac{1}{k_B T}$. That is, the probability to find the system with N particles and internal energy U .

Now, if we have an energy level ϵ_i , and n_i particles occupying that level, then:

$$\begin{aligned} N &= \sum_i n_i = n_1 + n_2 + n_3 + \dots \\ U &= \sum_i n_i \epsilon_i = n_1 \epsilon_1 + n_2 \epsilon_2 + n_3 \epsilon_3 + \dots \end{aligned}$$

That is, n_i is the number of ‘crosses’ on a particular energy level. Hence, Gibbs becomes:

$$\begin{aligned} P(N, U) &= \frac{e^{\beta(\mu \sum_i n_i - \sum_i n_i \epsilon_i)}}{\mathcal{Z}} \\ &= \frac{e^{\beta \sum_i n_i (\mu - \epsilon_i)}}{\mathcal{Z}} \end{aligned}$$

The Grand Partition Function \mathcal{Z} is the sum for n_i taking on all values (i.e. there being 1, 2, 3, ... particles in energy level 1, and again for all other energy levels). That is:

$$\begin{aligned} \mathcal{Z} &= \sum_{n_i} e^{\beta \sum_i n_i (\mu - \epsilon_i)} \\ &= \sum_{n_i} e^{\beta(n_1 \mu - n_1 \epsilon_1) + \beta(n_2 \mu - n_2 \epsilon_2) + \beta(n_3 \mu - n_3 \epsilon_3) + \dots} \\ &= \sum_{n_i} \prod_i e^{\beta(n_i \mu - n_i \epsilon_i)} \end{aligned}$$

So, $P(N, U)$ can be written:

$$\begin{aligned} P(N, U) &= \frac{e^{\beta \sum_i n_i (\mu - \epsilon_i)}}{\sum_{n_i} \prod_i e^{\beta(n_i \mu - n_i \epsilon_i)}} \\ &= \frac{\prod_i e^{\beta n_i (\mu - \epsilon_i)}}{\sum_{n_i} \prod_i e^{\beta(n_i \mu - n_i \epsilon_i)}} \\ &= \frac{e^{\beta n_1 (\mu - \epsilon_1)} e^{\beta n_2 (\mu - \epsilon_2)} e^{\beta n_3 (\mu - \epsilon_3)} \dots}{\sum_{n_i} e^{\beta n_1 (\mu - \epsilon_1)} e^{\beta n_2 (\mu - \epsilon_2)} e^{\beta n_3 (\mu - \epsilon_3)} \dots} \\ &= \frac{e^{\beta n_1 (\mu - \epsilon_1)}}{\sum_{n_1} e^{\beta n_1 (\mu - \epsilon_1)}} \frac{e^{\beta n_2 (\mu - \epsilon_2)}}{\sum_{n_2} e^{\beta n_2 (\mu - \epsilon_2)}} \frac{e^{\beta n_3 (\mu - \epsilon_3)}}{\sum_{n_3} e^{\beta n_3 (\mu - \epsilon_3)}} \dots \\ &= P(n_1, \epsilon_1) P(n_2, \epsilon_2) P(n_3, \epsilon_3) \dots \end{aligned}$$

So, the probability to find the system with N particles, and internal energy U is the product of the probabilities of finding n_i particles in energy level ϵ_i .

So, the average number of particles in energy level ϵ_i is given by:

$$\langle n(\epsilon_i) \rangle = \sum_{n_i=0,1,2,\dots} P(n_i, \epsilon_i) n_i$$

Where:

$$P(n_i, \epsilon_i) = \frac{e^{\beta n_i (\mu - \epsilon_i)}}{\sum_{n_i} e^{\beta n_i (\mu - \epsilon_i)}}$$

Let us suppose that we only allow either 0 or 1 particles in each energy state (i.e. fermionic case); hence:

$$\begin{aligned} \langle n(\epsilon_i) \rangle &= \sum_{n_i=0,1} P(n_i, \epsilon_i) n_i \\ &= 0 \times P(0, \epsilon_i) + 1 \times P(1, \epsilon_i) \\ &= 0 \times \frac{e^{\beta 0 (\mu - \epsilon_i)}}{\sum_{n=0,1} e^{\beta n (\mu - \epsilon_i)}} + 1 \times \frac{e^{\beta 1 (\mu - \epsilon_i)}}{\sum_{n=0,1} e^{\beta n (\mu - \epsilon_i)}} \\ &= \frac{e^{\beta (\mu - \epsilon_i)}}{e^0 + e^{\beta (\mu - \epsilon_i)}} \\ &= \frac{e^{\beta (\mu - \epsilon_i)}}{1 + e^{\beta (\mu - \epsilon_i)}} \\ &= \frac{1}{e^{\beta (\epsilon_i - \mu)} + 1} \end{aligned}$$

We have thus derived the Fermi-Dirac distribution.

Suppose that we allow any number of particles in each energy level; that is, n_i can take on any number $0, \dots, \infty$.

$$\begin{aligned} \langle n(\epsilon_i) \rangle &= \sum_{n_i=0}^{\infty} P(n_i, \epsilon_i) n_i \\ &= \frac{0 + e^{1\beta(\mu - \epsilon_i)} + 2e^{2\beta(\mu - \epsilon_i)} + \dots}{1 + e^{\beta(\mu - \epsilon_i)} + e^{2\beta(\mu - \epsilon_i)} + \dots} \end{aligned}$$

Here, we have noted that denominator (grand partition function) is actually a common factor to all expressions. To evaluate this sum, we see that this is actually:

$$\frac{a + 2a^2 + 3a^3 + \dots}{1 + a + a^2 + a^3 + \dots}$$

Now, the sum

$$\sum_{i=0}^{\infty} a^i = \frac{1}{1 - a},$$

is a standard result. We use this to find:

$$\langle n(\epsilon_i) \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}$$

We have thus derived the Bose-Einstein distribution.