Brief Notes on the Fermi-Dirac and Bose-Einstein Distributions, Bose-Einstein Condensates and Degenerate Fermi Gases

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(A)Basics of Statistical Thermodynamics

The Gibbs Factor

A system is assumed to be able to exchange both energy and particles with a reservoir. The probability that the system is in a specified quantum state is,

$$P(N,\varepsilon) \propto \exp\left\{\frac{(N\mu - E)}{kT}\right\} \tag{1}$$

k = Boltzmann's constant (1.38 x 10^{-23} Joules.^{o}K)

T = absolute temperature (^{o}K).

E = energy of the quantum state of N particles (Joules)

μ = chemical potential (illustrated below what this means), Joules

N = number of particles in the quantum state of interest.

Note: The probability is only proportional to the exponential expression, not equal to it. The actual probability results by normalising, that is,

$$P(N,\varepsilon) = \frac{1}{\Im}\exp\left\{\frac{(N\mu - E)}{kT}\right\} \tag{2}$$

where the **Grand Sum**, $\Im$, is found by summing the probabilities over all quantum states and over all possible numbers of particles,

$$\Im = \sum_{N=0}^{\infty}\sum_{states}\exp\left\{\frac{(N\mu - E)}{kT}\right\} \tag{3}$$

The Boltzmann Factor

This is a special case of the Gibb's factor when the number of particles is fixed, i.e. the system cannot exchange particles freely but can exchange energy with the reservoir. The probability that the system is in a specified quantum state is,

$$P(\varepsilon) \propto \exp\left\{-\frac{E}{kT}\right\} \tag{4}$$

The probability is only proportional to the exponential expression, not equal to it. The actual probability results by normalising, that is,

$$P(\varepsilon) = \frac{1}{Z}\exp\left\{-\frac{E}{kT}\right\} \tag{5}$$

where Z is known as the **Partition Function** and is found by summing the probabilities over all quantum states,

$$Z = \sum_{states}\exp\left\{-\frac{E}{kT}\right\} \tag{6}$$

Degeneracy / Density of States

The Gibbs and Boltzmann factors give probabilities for a specific quantum state. An energy level is **degenerate** if there is more than one quantum state with this energy. Suppose there are S(E) states with energy E. The probability of the system being in *any* state with energy E is,

(Diffusive contact): $$P(N,E) \propto S(E)\exp\left\{\frac{(N\mu - E)}{kT}\right\} \tag{7}$$

(Fixed number of particles): $$P(E) \propto S(E)\exp\left\{-\frac{E}{kT}\right\} \tag{8}$$

One important example of degeneracy is the energy states for a Schrodinger particle-in-a-box. The number of states with the same wavenumber, k (or, more precisely, the number of states with wavenumbers between k and k+dk) is,

$$S(k).dk = \frac{Vk^2}{2\pi^2}dk \tag{9}$$

where V is the volume of the box. This also applies for light (photons).

For non-relativistic particles of mass m, the number of states with the same energy level, E (or, more precisely, the number of states with energies between E and E+dE) is,

$$S(E).dE = \frac{V}{\sqrt{2}\pi^2} \cdot \frac{m^{3/2}}{\hbar^3} \cdot \sqrt{E} \cdot dE \tag{10}$$

Expressions (9) and (10) give the same number of states, just in terms of different variables. Equ.(10) follows from (9) by substituting $k^2 = 2mE/\hbar^2$. The function S is called the **density of states**. (The letter used for S varies between authors).

If the particles also have spin, then (9) or (10) must be multiplied by the number of spin states. E.g., for electrons or photons these expressions should be multiplied by 2.

(B) Derivation of the Fermi-Dirac Distribution

Fermions have half-integral spin and obey the Pauli Exclusion Principle, i.e. there cannot be more than one identical fermion in any single quantum state. If we consider a system consisting of just one quantum state, of energy ε, the Grand Sum becomes simple because the only possible numbers of particles are either 0 or 1. Hence (3) gives,

$$\Im = \sum_{N=0}^{1}\exp\left\{\frac{N(\mu-\varepsilon)}{kT}\right\} = 1 + \exp\left\{\frac{(\mu-\varepsilon)}{kT}\right\} \tag{11}$$

From (2) the probability of the state being occupied is the **Fermi-Dirac Distribution**,

$$P(\varepsilon) = \frac{\exp\left\{\frac{(\mu-\varepsilon)}{kT}\right\}}{1+\exp\left\{\frac{(\mu-\varepsilon)}{kT}\right\}} = \frac{1}{\exp\left\{\frac{(\varepsilon-\mu)}{kT}\right\}+1} \tag{12}$$

(C) Derivation of the Bose-Einstein Distibution

Bosons have integral spin. There can be any integral number of identical bosons in the same quantum state. In Equs.(1,2,3), the energy, E, is the energy of a quantum state of N particles. If the energy of a given quantum state is ε when occupied by one particle, the total energy for N particles in this state is $E = N\varepsilon$. We may consider just this one quantum state as the system in question, so the Grand Sum becomes,

$$\Im = \sum_{N=0}^{\infty} \exp\left\{-N\frac{(\varepsilon-\mu)}{kT}\right\} = \frac{1}{1-\xi} \tag{13}$$

Where,

$$\xi = \exp\left\{-\frac{(\varepsilon-\mu)}{kT}\right\} \tag{14}$$

The probability of the state being occupied by N particles is thus, from (2),

$$P(N,\varepsilon) = (1-\xi)\exp\left\{-\frac{N(\varepsilon-\mu)}{kT}\right\} = (1-\xi)\xi^N \tag{15}$$

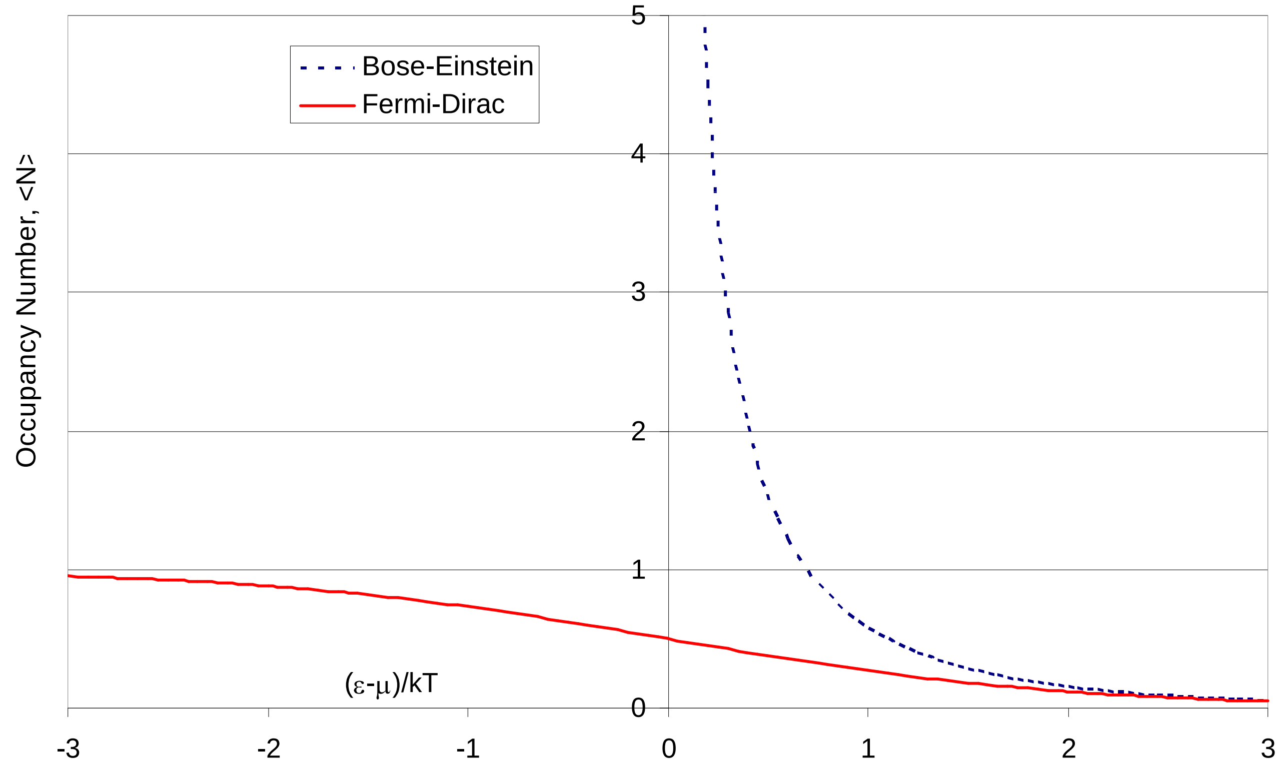
The expectation value for the number of particles in this state of energy ε is thus,

$$\begin{aligned}\langle N\rangle &= \sum_{N=0}^{\infty} NP(N,\varepsilon) = \sum_{N=0}^{\infty} N(1-\xi)\xi^N = (1-\xi)\xi\sum_{N=0}^{\infty} N\xi^{N-1} \\ &= (1-\xi)\xi\frac{d}{d\xi}\sum_{N=0}^{\infty}\xi^N = (1-\xi)\xi\frac{d}{d\xi}\left(\frac{1}{1-\xi}\right) = (1-\xi)\xi\cdot\frac{1}{(1-\xi)^2} \\ &= \frac{\xi}{1-\xi} = \frac{1}{1/\xi-1} = \frac{1}{\exp\left\{\frac{(\varepsilon-\mu)}{kT}\right\}-1}\end{aligned} \tag{16}$$

This is the **Bose-Einstein Distribution**. It differs from the Fermi-Dirac distribution only as regards the sign of the “1” in the denominator. But this difference is crucial.

For the Bose-Einstein distribution, the chemical potential, μ, must be less than the lowest energy level, ε_0, i.e. $\mu \le \varepsilon_0$, so that ε-μ cannot be negative. This differs from the Fermi-Dirac distribution for which the chemical potential may exceed the lowest energy state and ε-μ may be negative. The two distributions are plotted against (ε-μ)/kT below. Salient features are,

- The two distributions become essentially the same for (ε-μ)/kT > 3;
- For bosons the occupation number becomes infinite as (ε-μ)/kT tends to zero;
- This means that there will be very large numbers of bosons in any state whose energy (strictly ε-μ) is small compared with kT;
- For fermions the mean occupation number is ½ when (ε-μ)/kT = 0;
- This means that about half the states whose energy (strictly ε-μ) is small compared with kT will be occupied by a fermion;
- For fermions the mean occupation number tends to 1 when (ε-μ)/kT becomes large and negative.
- This means that as absolute zero is approached, all those states with ε < μ will be occupied by a fermion.



(D) Bose-Einstein Condensates

As the temperature of a system of bosons is reduced the value of (ε-μ)/kT will become large and positive for any states with ε > μ. Consequently the mean occupation number will become very small for all such states. If there is a fixed number of bosons, it follows that they must all end up in states with ε = μ. Consequently, at absolute zero the value of the chemical potential for a system of bosons must equal the ground state energy, $\mu = \varepsilon_0$. Moreover, at absolute zero we expect all the bosons to end up in the ground state (noting that for ε = μ the occupation number is divergent).

In a sense, therefore, there is nothing surprising about Bose-Einstein condensation. The Bose-Einstein condensate phase of a Bose gas consists simply of a large proportion of the bosons in the ground state. However, the surprising thing is that the onset of Bose-Einstein condensation is quite sudden (i.e. it is a phase change) and occurs well above absolute zero (e.g. at a temperature of 2.17K for helium-4[1]). A simple theoretical expression for the critical temperature for the onset of Bose-Einstein condensation is derived as follows:-

Since $\mu = \varepsilon_0$ at absolute zero we approximate $\mu = \varepsilon_0 - \mu_1 kT$ at sufficiently low temperatures, so that $\exp\left\{\frac{(\varepsilon - \mu)}{kT}\right\} = e^{\mu_1}$ for the ground state. The mean occupancy of the ground state is thus, from (16), $\langle N_0 \rangle = \frac{1}{e^{\mu_1} - 1}$, where the subscript $_0$ denotes the

[1] Helium-4 consists of 2 protons, 2 neutrons and 2 electrons, and hence has an even number of fermions. Overall it has spin zero, and hence is a boson.

ground state. From this we see that the temperature derivative of the chemical potential of a boson gas at low temperature, $\frac{\partial \mu}{\partial T} = -k\mu_1$, determines the occupancy of the ground state.

Re-arranging gives $e^{\mu_1} = 1 + \frac{1}{\langle N_0 \rangle}$. At absolute zero we expect all the particles to end up in the ground state, so that $\langle N_0 \rangle \to N$ at low temperatures, where N is the total number of bosons. Hence, if the number of particles is very large, e^{μ_1} must be extremely close to 1. Using this approximation, (16) gives the mean occupation number of any excited state (i.e. above the ground state) to be simply,

$$\langle N_\varepsilon \rangle = \frac{1}{\exp\left\{\frac{\varepsilon_1}{kT}\right\} - 1} \tag{17}$$

where $\varepsilon_1 = \varepsilon - \varepsilon_0$ is the energy of the state with respect to the ground state. Hence, if the first excited state has a (relative) energy which is much larger than kT, i.e., if $\varepsilon_1 >> kT$, then the mean occupancy of the excited state will be small, << 1.

We want to know the total number of bosons in all excited states. For this we need to know how many states there are, not just their energies. This information is provided by the density of states, Equ.(10). NB: In using this form of density of states we are restricting attention to *massive* bosons, not photons. The expected number of particles with energy between ε and ε+dε is the number of states in this range times the mean occupancy, $\langle N_\varepsilon \rangle$, of each, giving,

$$dN_e(\varepsilon) = \frac{V}{\sqrt{2}\pi^2} \cdot \frac{m^{3/2}}{\hbar^3} \cdot \frac{\sqrt{\varepsilon} \cdot d\varepsilon}{\exp\left\{\frac{\varepsilon_1}{kT}\right\} - 1} \tag{18}$$

We have changed the notation slightly to emphasise that the LHS (dN_e) means the total number of particles in this energy range, not just the occupancy of a single quantum state. To make things a little simpler, it is usual to assume that we are dealing with excited state energies which are quite a bit higher than the ground state energy, so that we can ignore the distinction between ε_1 and ε. Changing the variable in (18) to $x = \varepsilon / kT$ then gives,

$$dN_e(\varepsilon) = \frac{V}{\sqrt{2}\pi^2} \cdot \frac{(mkT)^{3/2}}{\hbar^3} \cdot \frac{\sqrt{x} \cdot dx}{e^x - 1} \tag{19}$$

The total number of particles in all excited states (i.e. not including the ground state) is found by integration to be,

$$N_e = V \cdot \frac{(mkT)^{3/2}}{\hbar^3} \cdot \frac{1}{\sqrt{2}\pi^2} \int_0^\infty \frac{\sqrt{x} \cdot dx}{e^x - 1} \tag{20}$$

Consistent with previous approximations the lower limit of the integral is set to zero, though really it should be a small finite value (i.e. the gap between the ground state and the first excited state). The last part of (20) is just a numerical constant which can be evaluated numerically to be,

$$\frac{1}{\sqrt{2}\pi^2}\int_0^\infty \frac{\sqrt{x}\cdot dx}{e^x-1} = 0.1659 \tag{21}$$

The total particle number density is $\rho_N = N/V$, where N is the total number of particles. Hence, on dividing by N, Equ.(20) gives the *fraction* of the particles in excited states to be,

$$\frac{N_e}{N} = 0.1659\frac{(mkT)^{3/2}}{\hbar^3\rho_N} \tag{22}$$

Clearly this only makes sense if the RHS evaluates to a number less than 1. When it does not, then the assumptions of the derivation have broken down. When it evaluates to less than 1, the remainder of the particles must be in the ground state. Thus, the fraction of particles in the ground state is,

$$\frac{N_0}{N} = 1-\frac{N_e}{N} = 1-0.1659\frac{(mkT)^{3/2}}{\hbar^3\rho_N} \tag{23}$$

Pause to reflect how extraordinary this is. Equ.(23) means that a substantial fraction of all the particles are in the ground state. In other words, a substantial fraction of the boson gas is in a new (superfluid) phase. This is true if the RHS of (23) is positive, i.e. if,

$$0.1659\frac{(mkT)^{3/2}}{\hbar^3\rho_N} < 1 \tag{24}$$

Solving for the critical temperature for Bose-Einstein condensation (BEC) gives,

$$kT_{BEC} = 3.313\frac{\hbar^2}{m}\rho_N^{2/3} \tag{25}$$

Thus, the onset of Bose-Einstein condensation will be at a higher temperature if,

- The number density of particles is greater, or,
- The particles are lighter.

Example: Helium-4:

Number density of liquid He^4 is 2.18 x 10^{28} m^{-3}, and the mass of an He^4 atom is 6.68 x 10^{-27} kg. Hence,

$$kT_{BEC} = 3.313\frac{\left(1.054x10^{-34}\right)^2\left(2.18x10^{28}\right)^{2/3}}{6.68x10^{-27}} = 4.3x10^{-23}\,J$$

Using k = 1.38x10^{-23} J^oK gives T_{BEC} = 3.1^{o}K. This is a pretty reasonable estimate given that the onset of the superfluid phase of He^4 is found to occur at 2.17^{o}K.

(E) Degenerate Fermi Gases (Non-Relativistic)

Recall the appearance of the Fermi-Dirac distribution - see above graph and Equ.(12). Re-iterating some of the salient features of the distribution, and making some conclusions…

- For fermions the mean occupation number tends to 1 when (ε-μ)/kT becomes large and negative.
- This means that as absolute zero is approached, all those states with ε < μ will be occupied by a fermion.
- The value of the chemical potential, μ, of a fermion at absolute zero is known as the **Fermi Energy**, ε_F.
- At sufficiently low temperatures, specifically when kT << ε_F, virtually all the states with energies below ε_F will be occupied, and virtually no states with energies above ε_F will be occupied.
- A fermion gas with kT << ε_F, is said to be **degenerate**.

The value of the Fermi energy is easily evaluated. From Equ.(10) the total number of quantum states with energies less than or equal to ε_F is,

$$N(\varepsilon \le \varepsilon_F) = 2\frac{V}{\sqrt{2}\pi^2}\cdot\frac{m^{3/2}}{\hbar^3}\int_0^{\varepsilon_F}\sqrt{E}\cdot dE = \frac{2\sqrt{2}V}{3\pi^2}\cdot\frac{m^{3/2}}{\hbar^3}\cdot\varepsilon_F^{3/2} \qquad (26)$$

where we have multiplied (10) by 2 to account for the two spins states of a spin ½ fermion. The Fermi energy is, by definition, the energy for which the number of states with energies not exceeding this level equals the number of fermions present. In terms of the number density of fermions, $\rho_N = N/V$, Equ.(26) re-arranges to give the Fermi energy as,

$$\varepsilon_F = 4.785\frac{\hbar^2}{m}\rho_N^{2/3} \qquad (27)$$

Note that Equ.(27) for the Fermi energy is almost the same as Equ.(25) for the energy at the onset of Bose-Einstein condensation, apart from the constant factor (though only one can be relevant for any given particle type, of course).

Example 1: Electrons in Metals

For copper, $\rho_N = 8,.5x10^{28}m^{-3}$ and the electron mass is m = 9.1 x 10^{-31} kg, giving,

$$\varepsilon_F = 4.785\frac{(1.054\times10^{-34})^2(8.5\times10^{28})^{2/3}}{9.1\times10^{-31}} = 1.1\times10^{-18}J = 7eV$$

Hence, using k = 1.38x10^{-23} J^{o}K gives the Fermi temperature, $T_F = \varepsilon_F/k$, to be 82,000^{o}K. Consequently the electrons in metals are well degenerate, i.e. temperatures below the melting point are much smaller than T_F.

Given that Equs.(25) and (27) for T_{BEC} and T_F are so similar, why is the He^4 BEC temperature as low as ~3^{o}K but T_F for electrons in metals is so high? The answer is simply because of the factor of 7,340 mass difference between the He^4 atom and an electron.

Example 2: Helium-3

He^3 consists of two protons, one neutron and two electrons. It therefore has an odd number of fermion constituents and must be a fermion. (It has spin ½). Hence He^3 is a very different beast from He^4 since the latter is a boson. The similarity of Equs.(25) and (27), and the similarity of the masses of He^3 and He^4, imply that we should expect a gas of He^3 to be a degenerate Fermi gas at temperatures below, very roughly, ~1^{o}K or so. This is indeed found to be the case (for example by measuring its specific heat).

Example 3: White Dwarfs

White dwarfs are the end point of the evolution of stars in a certain range of initial masses. They have a mass comparable to the Sun, but with linear dimensions about 100 times smaller, and hence have a mean density about a million times greater, with $\rho_N \sim 10^{36} m^{-3}$. The material of a white dwarf is entirely ionised into nuclei and free electrons. The Fermi temperature for the electron gas is thus,

$$T_F \sim 4.785 \frac{\left(1.054\times10^{-34}\right)^2 \left(10^{36}\right)^{2/3}}{\left(1.38\times10^{-23}\right)\left(9.1\times10^{-31}\right)} = 4\times10^9 K \qquad (\varepsilon_F = 0.37 \text{ MeV})$$

The temperature in the interior of a white dwarf is probably around 10^7K, and certainly not more than ~10^8K, so the electron gas is degenerate. In fact, it is the degeneracy pressure of the degenerate electron gas which prevents the white dwarf collapsing further under the action of gravity.

Note that the Fermi energy is comparable with the rest mass energy of an electron (0.511 MeV) so that these electrons are becoming relativistic and the calculation is only just valid. It is this fact that limits the possible size of white dwarfs. Repeating the calculation relativistically reveals that electron degeneracy pressure can support the star against gravitational collapse only if its mass is below a certain limit, which is about 1.46 times the solar mass. Consequently, stars with greater mass than this remaining at the end of their evolution are doomed to be crushed by gravity into an even more dense state – a neutron star, a quark star or a black hole.

Finally, are the protons in a white dwarf degenerate? Their Fermi temperature differs from that of the electrons only by the ratio of their masses, 1836, so $T_F \sim 2 \times 10^6$K. This is rather less than the likely temperature in the centre of the white dwarf, and so the protons are probably not degenerate. Consequently the protons do not contribute significantly to supporting the star against gravitational collapse.