

6. QUANTUM & CLASSICAL IDEAL GASES

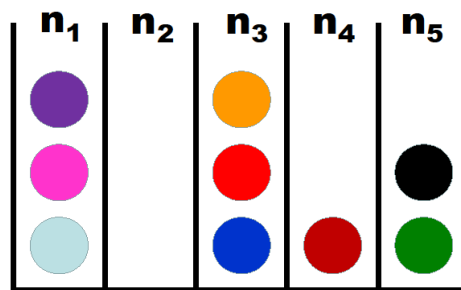
GOAL: To derive some key properties of non-interacting Fermi and Bose gases, and show how in the limit of low density and/or high temperature these gases behave like a classical “Maxwell-Boltzmann” gas

In this section we seriously address for the first time the consequences of indistinguishability for multi-particle quantum systems. In 3 dimensions we can have either Bose or Fermion statistics, and the results at low temperatures or high densities, even for non-interacting gases, are completely different from those we would get for a classical gas of distinguishable particles.

6(a) Quantum Statistics

Suppose we have a set of N non-interacting particles which can exist in one of a set of m different 1-particle states, which we label ϕ_α , with $\alpha = 1, 2, \dots, m$. Suppose also that these particles are *distinguishable* (we can, eg., imagine them having different colours). Then a possible situation is as shown in the figure below, where we imagine that we have an N -particle state in which there are n_1 particles in the 1-particle state ϕ_1 , n_2 particles in state ϕ_2 , etc.; we have $\sum_\alpha n_\alpha = N$.

Examples of such 1-particle states abound. For example, if we have electrons bound to an atom, and we assume that the electrons don't interact with each other, then the *quantum numbers* α for the electrons (ie., the list of the different possible 1-electron states are just n , l , m , and σ , where n is the radial quantum



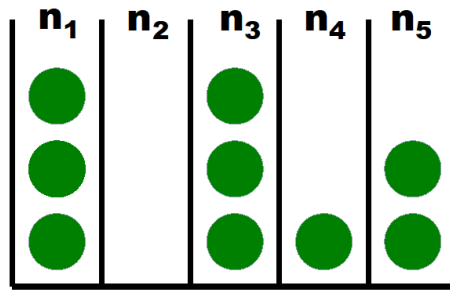
number, l the orbital quantum number, and m the projection of the angular momentum along the z axis; and σ is the spin quantum number. If we ignore n , l , and m (eg., by supposing the electrons are all in the s state), then we have only σ left; for a spin-half electron this means that there are only 2 boxes in the figure above (spin up and spin down). Another example – the set of allowed states for a particle in a 3-d box, where the quantum numbers are just the allowed momenta.

Let us now ask how many different possible *distinguishable* states correspond to the situation shown in this figure, in which the only thing we stipulate is that there are n_α particles in the α -th cell (where in the figure, $N = 9$, and $n_1 = 3$, $n_2 = 0$, and so on). It is easy to see that the total number of different distinguishable states, or the “multiplicity” of states $\Omega_N(\{n_\alpha\})$ corresponding to this stipulation, is actually the multinomial function, i.e., we have

$$\Omega_N(\{n_\alpha\}) = C^N_{\{n_\alpha\}} = N! / \prod_\alpha n_\alpha! \quad (\text{distinguishable}) \quad (1)$$

where \prod_α signifies we take the product over all the α (compare probability notes, equation (1)). We see that (1) is true by noting that we can permute the N balls a total of $N!$ ways between all the different cells; but permutations inside the α -th cell change nothing, since all they do is change the internal ordering of the balls in this cell, while still keeping the $\{n_\alpha\}$ the same. For the particular case shown we have $\Omega_N(\{n_\alpha\}) = 9! / (3! \cdot 0! \cdot 3! \cdot 1! \cdot 2!) = 362,880 / 72 = 5,040$ different possible arrangements equivalent to the figure (i.e., having the same occupation numbers).

Now suppose the particles are *indistinguishable*. Then we have the quite different situation shown in the figure below, where we have all the balls with the same colour:



Now we have a quite different situation, because any permutations are quite irrelevant here – in fact, we entirely specify the state in the figure by simply giving the list of occupation numbers $\{n_j\}$, and there is only ONE state with this set of occupation numbers. Thus in this case we have

$$\Omega_N(\{n_j\}) = 1 \quad (\text{indistinguishable}) \quad (2)$$

Thus we arrive at the following conclusion. If we have a set of distinguishable particles whose state is defined by specifying the set $\{n_\alpha\}$ of occupation numbers, then there is a large multiplicity of such states, given by eqn (1). On the other hand if the particles are indistinguishable, then there is only one possible state with a given set $\{n_\alpha\}$, i.e., eqn (2) is obeyed.

Quantum Mechanics for many particles: In QM there is one other crucial consequence of indistinguishability. This is that the occupation numbers of each state are not arbitrary. Let’s recal some basic results about the effect of indistinguishability in QM (which can be found in any QM text book). The key result to be derived is that in 3 dimensions there are only two different possibilities for the allowed occupation numbers, corresponding to fermionic or bosonic statistics; for fermions, we can only have an

occupation of 0 or 1 for an individual state, whereas for bosons we can occupy a given state with as many particles as we want.

Actually, this is not the end of the story. In other dimensions things are different – in 2 dimensions we can have “anyons”, with an arbitrary statistical parameter, and in 1 dimension statistics are not well defined. To discuss this requires techniques beyond the scope of this course.

Let us recall how things work in 3 dimensions. To begin, consider two *distinguishable* particles (with coordinates labeled by $\mathbf{r}_1 = 1$ and $\mathbf{r}_2 = 2$) occupying two single particle states ϕ_A and ϕ_B . Now if the particles are not in any way correlated, we can certainly write down a state of form $\psi_{AB}(1,2) = \phi_A(1)\phi_B(2)$, in which the “first particle” (ie., the one at position \mathbf{r}_1) is in state ϕ_A , and the second one is in state ϕ_B .

Now suppose the particles are indistinguishable. Then this means that, from the fundamental physical standpoint, there is no difference whatsoever between the state $\psi_{AB}(1,2) = \phi_A(1)\phi_B(2)$ and the state $\psi_{BA}(1,2) = \phi_A(2)\phi_B(1)$, in which we have swapped the particle coordinates between the states A and B.

There are now 2 ways (at least) that we can proceed in our argument. The first is the one you have probably learnt in a QM course. This argument is pretty simple – it points out that the probability density $|\Psi|^2$ should be well defined. Now if we write a wave function like $\psi_{AB}(1,2)$ for the pair of states, this is not the case – for this state is supposed to be indistinguishable from $\psi_{BA}(1,2)$, which is supposed to represent the SAME physical state. Clearly however it is not, because $|\Psi|^2$ is *not* the same for the 2 states (to see this, suppose that state A is strongly localized around its coordinate, whereas state B is spread out around its coordinate – then clearly $|\psi_{AB}(1,2)|^2$ is not the same as $|\psi_{BA}(1,2)|^2$, as a function of the coordinates $\mathbf{r}_1 = 1$ and \mathbf{r}_2).

However there are 2 states that do fit the bill. To see what they might be, note first that to satisfy the “exchange symmetry” relation $|\Psi(1,2)|^2 = |\Psi(2,1)|^2$, we can have either $\Psi(1,2) = \Psi(2,1)$, or $\Psi(1,2) = -\Psi(2,1)$. We then see that we can have one of two possible states for the pair wave-function involving one particle states ϕ_A and ϕ_B . These are

$$\Psi(1,2) = \frac{1}{\sqrt{2}}[\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] \quad (\text{bosons}) \quad (3)$$

$$\Psi(1,2) = \frac{1}{\sqrt{2}}[\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)] \quad (\text{fermions}) \quad (4)$$

There is actually a much faster way of getting this result, as follows. We note that in QM, the total wave-function can be composed of superpositions, with arbitrary coefficients, of all possible states that are solutions of the relevant Hamiltonian with appropriate boundary conditions. In the present case, we only have 2 states A and B, and to get the right coefficients here we invoke the exchange symmetry requirement above – clearly a wave function of form $\Psi(1,2) \sim [\phi_A(1)\phi_B(2) + e^{i\theta}\phi_A(2)\phi_B(1)]$ will fit the bill, and then to satisfy the condition $|\Psi(1,2)|^2 = |\Psi(2,1)|^2$, we see that we must have either $\theta = 0$ or $\theta = \pi$.

A far more general approach to this can be found by using the path integral approach to QM. To see the derivation using these techniques, see the opening chapter of the book “Path Integrals in Quantum Mechanics”, by RP Feynman and AR Hibbs. If this derivation is repeated in 2 dimensions, one finds that one is no longer restricted to boson or fermions statistics – one can have “anyon statistics”. In one dimension, it turns out that the notion of statistics for the particles is not even well defined in QM.

All the discussion so far is for 1-particle and 2-particle states, and implicit in this discussion is that the particles are not interacting with each other. Now for a general multi-particle system in which there **are** interactions between the particles, we cannot expect the states to be single particle states. In this more general case, the states will be some set $\{\Phi_k(1,2,\dots,N)\}$, where N is the number of particles and the coordinates are labeled as above, by the particle number (thus, in non-relativistic QM, we would write $1 = (\mathbf{r}_1, \sigma_1)$, where \mathbf{r}_1 is the position of the particle and σ_1 its spin state, $2 = (\mathbf{r}_2, \sigma_2)$,; and so on). These states will in general look very complicated, and it will not be possible to specify them by specifying the occupation n_α of the single-particle states ϕ_α . Note that the number of multi-particle states here is vastly larger than the number of 1-particle states. In fact, if we have m different 1-particle states, we can expect that the number M of multi-particle states will be $M = m^N$, when we have N particles.

Suppose, however, that we have an **ideal gas** of quantum particles, ie., one on which there are no interactions between the particles. In this case, the energy of any particular particle is independent of what any of the other particles are doing, and we may assign a 1-particle energy ε_j to this particle if it is state ϕ_j . The total energy is then just sum of all the single particle energies. Of course this is an approximation since whenever particles interact their QM wave-functions and energies are perturbed. Nevertheless this approximation works remarkably well in describing many real systems. (in particular, real dilute gases, or gases at high T , where $k_B T \gg |V_{ij}|$ and V_{ij} is the interaction between particles i and j ; or gases of photons, or of phonons in a solid, liquid, or gas, etc.). It then follows that

The macrostate of an ideal gas may be specified by giving the mean occupancy $\langle n(E) \rangle$ for all single-particle states.

This simplifies things enormously! Instead of the vast Hilbert space of the N -particle states, we only have to deal with 1-particle states. We now wish to look a little more at the behaviour of a set of N non-interacting quantum particles, in 3 dimensions.

6(a) Fermi & Bose Distribution Functions

We have just seen that if we want to specify the state of a quantum system of indistinguishable particles, all we have to do is fix the allowed states, and then fix the occupation numbers in each state - this is enough to completely specify the state. We now wish to consider the case of an ideal gas. Then, as we have seen, all we have to do is define the allowed 1-particle states ϕ_α and then fix the occupation numbers n_α in each 1-particle state, in order to completely fix the N -particle state for the system.

For this case of the ideal gas, let us define the **1-particle distribution function over energy**, as the mean occupancy as function of single particle energy E .

$$f(E) \equiv \langle n(E) \rangle \quad (5)$$

Note that this is a not a probability distribution over states, but over energies. We can also define a probability distribution $f(\alpha)$ over the set of states $\{\alpha\}$, in the same way, ie.,

$$f(\alpha) = \langle n(\alpha) \rangle \quad (6)$$

If there is multiple degeneracy of states at a given E , then clearly these 2 distribution function will not be the same. We will see very soon why we choose to deal with a distribution over energy.

We are going to do things in the grand canonical ensemble. One might wonder why this is – there are 2 reasons:

- First, the behaviour of the system often depends in an important way on the chemical potential and/or the number of particles
- Second, it turns out to be much easier to do calculations in the grand canonical ensemble than in the canonical ensemble.

Thus, we will assume that in general the distribution function $f(E, \mu, T)$ depends on the temperature and chemical potential. It also depends on the type of particle one is dealing with (fermion or boson) since the occupancy is limited to be either 0 or 1 in the case of fermions, whereas in the case of bosons there is no such limit.

In what follows we will deal with both Fermi and Bose gases. We will also look at the classical limit, where both Fermi and Bose gases have the behavior of a **classical** ideal gas. A classical ideal gas is defined as a set of particles for which the mean *occupation number* n for all single particle states is much less than 1. In other words $f(E) \ll 1$ for all E . A classical ideal gas is often described as being “*non-degenerate*”. In such a gas we will see that $f(E)$ is proportional to $\exp[-E/k_B T]$. This looks similar to the canonical distribution function $p(E_i)$ which is also proportional to the Boltzmann factor. $\exp[-E/k_B T]$. This is because in an ideal gas the probability that two particles are in the same state is negligibly small.

(i) Fermi-Dirac Distribution

Consider a single fermionic state with energy E in contact with a reservoir of fermions at temperature T and chemical potential μ . Assuming zero energy corresponds to the empty state; the grand partition function for this single state is then

$$\Xi = \sum_{n=0}^1 \exp[\beta(n\mu - E(n))] = 1 + \exp[\beta(\mu - E)] \quad (7)$$

where the first term corresponds to $n = 0$ and the second term to $n = 1$. We can write this somewhat differently, by writing it explicitly for the state α , with energy E_α ; we then have

$$\Xi_\alpha(\beta, \mu) = 1 + \exp[\beta(\mu - E_\alpha)] \quad (8)$$

The advantage of writing it in this form is that we can then immediately write the grand partition function over all the different states $\{\alpha\}$; since we deal with an ideal gas, so that these states are not coupled to each other, this is just

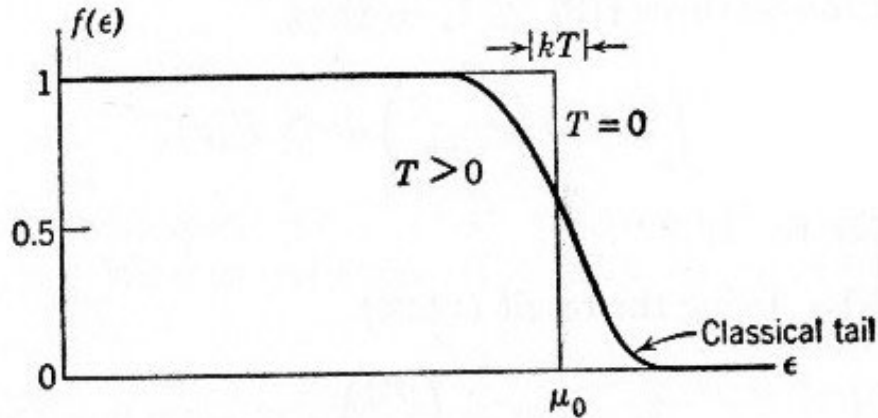
$$\Xi(\beta, \mu) = \prod_\alpha \Xi_\alpha(\beta, \mu) = \prod_\alpha (1 + \exp[\beta(\mu - E_\alpha)]) \quad (9)$$

ie., the product over all the different states of the partition function for each state.

We may immediately find the mean occupancy of a state with energy E in the form

$$f(E) = \langle n \rangle = \Xi^{-1} \sum_n n \exp[\beta(n\mu - E(n))] = \frac{\exp[\beta(\mu - E)]}{1 + \exp[\beta(\mu - E)]} = \frac{1}{1 + \exp[\beta(E - \mu)]} \quad (10)$$

This distribution function, or occupancy function, is called the Fermi-Dirac or just the “fermionic” distribution function. It is easy to plot it as a function of energy – we show it here for the case $T = 0$, and for a finite T with $k_B T \sim 0.1\mu_0$, where μ_0 is the chemical potential for $T = 0$.



Note that for most of the energy range, $f(E)$ is not small – however for energies E such that $E - \mu_0 \gg k_B T$, we do have $f(E) \ll 1$ (indeed, exponentially small), and so the particles in this energy range do behave classically. At low temperatures when $k_B T \ll \mu$ and $f(E)$ for a Fermi gas is close to 1 for $E < \mu$, the system is often called a *degenerate* Fermi gas. In the opposite high- T limit we refer to a *non-degenerate* Fermi gas.

Note also that it is very common to refer to the empty states below the chemical potential here as “holes”, ie., we refer to the distribution function $(1 - f(E))$ as the *hole distribution function*, for states below the chemical potential. Another common term employed in this business is the “Fermi energy”, often labeled as E_F , which is just another name, for fermions, for the $T = 0$ chemical potential μ_0 .

Now in general we can have conditions, in a real system, where both the chemical potential and the particle number allowed to vary. Thus if, for example, we connect a semiconductor (which has a very low density of free electrons) to an external voltage, then the chemical potential will depend on the voltage, and electrons can also flow in or out the wire connecting the metal to the voltage source – thus both N and μ are variable. It will be immediately obvious (and we will study this in some detail in a later chapter) that the chemical potential will also depend on temperature and on density – so we have a complicated problem!

Let us therefore begin here by simplifying things, by stipulating that the system contains a fixed number N of fermions (this would be the case for a metal or semiconductor disconnected from any charge source, or for the fermions in a neutron star). This then allows us to fix the chemical potential since it is the remaining free

$\rho = N/V$ and of the temperature of the heat bath, but we can now make precise statements. If $g(E)$ is the density of states, i.e. the number of states per unit volume V in the interval $(E, E + dE)$ then $\mu(T, \rho)$ is determined by solving the transcendental equation:

$$N = \int_0^{\infty} Vg(E)f(E, \mu, T)dE = V\rho \quad (11)$$

The Fermi energy, defined as $\mu(T = 0)$ is then obtained from the implicit equation:

$$\rho = \int_0^{E_F} g(E)dE \quad (12)$$

Setting $T = 0$ in eqtn. (11), we find for a 3d gas that

$$N = V \int_0^{E_F} g(E)dE = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{E_F} E^{1/2} dE = \frac{V}{3\pi^2} \left(\frac{2mE_F}{\hbar^2} \right)^{3/2} \quad (13)$$

where we have multiplied our density of states by a factor $2S + 1 = 2$ assuming our fermions are spin $1/2$, as in the case of electrons.

Solving for E_F in this equation we get the $T=0$ result

$$E_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3} \quad (14)$$

This result defines the “**Fermi surface**” defined by the set of all states in k -space lying at the Fermi energy; thus for a Fermi gas it is a sphere. One can also define a Fermi temperature from $E_F = k_B T_F$, and a Fermi wave vector $E_F = (\hbar k_F)^2 / 2m$, which is the radius of the Fermi surface. Finally, for this free gas, we can define a Fermi velocity by $E_F = \frac{1}{2} m v_F^2$.

At finite T we must solve equation (11) numerically (although one can also do things analytically, it is rather complicated). One finds that the chemical potential at low T is positive for a 3d Fermi gas – however a temperature roughly equal to E_F , it goes negative, and the high- T limiting behavior has increasingly negative $\mu(T)$. This is because at high T , minimization of the free energy is accomplished by maximizing the entropy S . We return to this topic at the end of this chapter.

(ii) Bose Einstein Distribution

Now consider a microsystem with a single bosonic state in contact with a reservoir with chemical potential μ and temperature T . As before, we are going to have to determine $\mu(T)$ from a self-consistency equation. The grand partition function in this case is:

$$\begin{aligned}\Xi &= \sum_{n=0}^{\infty} \exp[\beta(n\mu - E(n))] = \sum_{n=0}^{\infty} \exp[\beta(n\mu - nE)] = \sum_{n=0}^{\infty} (\exp[\beta(\mu - E)])^n \\ &= \frac{1}{1 - \exp[\beta(\mu - E)]}\end{aligned}\quad (15)$$

Again, we can write this explicitly for some state α , having energy E_α , in the form

$$\Xi_\alpha(\beta, \mu) = (1 - \exp[\beta(\mu - E_\alpha)])^{-1} \quad (16)$$

and we can again immediately write the grand partition function over all the different states $\{\alpha\}$; again, for an ideal gas these states are not coupled to each other, and so we get

$$\Xi(\beta, \mu) = \prod_\alpha \Xi_\alpha(\beta, \mu) = \prod_\alpha (1 - \exp[\beta(\mu - E_\alpha)])^{-1} \quad (17)$$

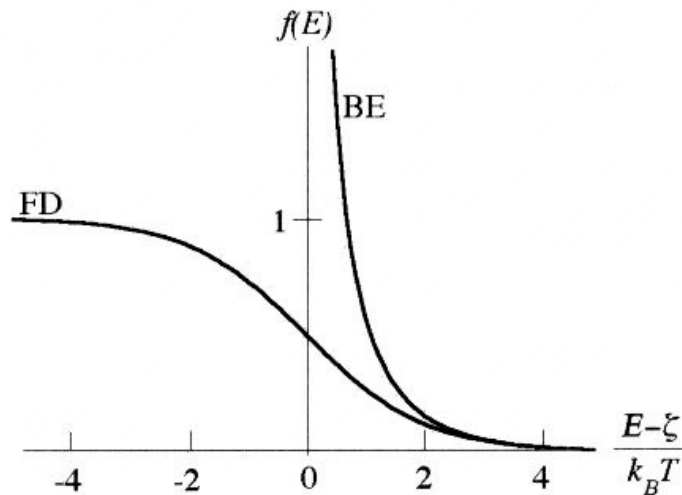
ie., the product over all the different states of the partition function for each state.

In the same way as for fermions, we then find that the mean occupation number for this energy is then:

$$\begin{aligned}f(E) = \langle n \rangle &= \beta^{-1} \Xi^{-1} \left(\frac{\partial \Xi}{\partial \mu} \right)_T = \beta^{-1} \Xi^{-1} (-\Xi^2) (-\beta \exp[\beta(\mu - E)]) = \frac{\exp[\beta(\mu - E)]}{1 - \exp[\beta(\mu - E)]} \\ &= \frac{1}{\exp[-\beta\mu] \exp[\beta E] - 1} = \frac{1}{\alpha^{-1} \exp[\beta E] - 1}\end{aligned}\quad (18)$$

where α is as usual the activity.

We can plot this distribution and compare it with the Fermi distribution. It is remarkable what difference a sign makes! The plot shown below is depicted as a function of the dimensionless ratio of energy divided by temperature, to give a fair comparison.



Note here that whereas the Fermi distribution $\langle n(E) \rangle$ is well defined for $E - \mu$ both positive and negative, the Bose distribution $\langle n(E) \rangle$ is only well defined if $E - \mu$ is positive, and it diverges as $\mu \rightarrow E$ from below. This is because if $\mu > E$ it is favourable for a boson to move from the particle reservoir into the level, no matter how many bosons are already there. This is evident from the observation that the Gibb's factor increases monotonically as a function of n when $\mu > E$. Thus there can be no equilibrium if $\mu > E$.

Since typically we are dealing with systems where the ground state energy is defined to be zero this means that in the Bose distribution, we must have $\mu < 0$. As in the case of fermions, if a system with a fixed particle number N is brought into contact with a heat bath at temperature T , the system will equilibrate according to the Bose distribution with a μ determined by N and T .

We will see later on that the results for non-interacting bosons depend very strongly on whether they are massive or not. Massless bosons like photons do not have a conserved number – we can create or destroy photons at will. The same is also true for many of the bosonic excitations in condensed matter systems, like phonons or magnons (quantized spin waves). As we will see, this non-conservation of boson number forces the chemical potential to be zero.

On the other hand massive bosons like bosonic atoms do conserve number, and they behave in a very different way – we will find that the chemical potential is usually negative unless they undergo Bose condensation. This is discussed in a later chapter.

Finally, let us consider how we may determine the chemical potential as a function of density and temperature; just as we did for the Fermi gas, we can do this by fixing the total particle number. As for equation (11) above, we write, assuming a continuous density of states $g(E)$, that

$$N \approx V \int_0^{\infty} \frac{g(E)}{\exp[\beta(E - \mu)] - 1} dE \quad (19)$$

Using the 3D density of states for a particle in a box, as before, we have

$$g(E) = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} \quad (20)$$

and changing variables to $x = \beta E$ this integral can be written:

$$N = \frac{V}{4\pi^2} \left(\frac{2mk_B T}{\hbar^2} \right)^{3/2} \int_0^{\infty} \frac{x^{1/2}}{\exp[x - \beta\mu] - 1} dx \quad (21)$$

Thus given, N , T and V one can in principle solve this equation to obtain μ . This is possible *if* N is not too large. However, there is an inconsistency here - no solution to (21) exists if N exceeds a certain critical value N_{cr} , because the integral has a maximum value of $1.36\pi^{1/2}$ as a function of μ . The maximum occurs when $\mu \rightarrow 0$. (recall we have just seen that the Bose distribution is only defined for $\mu < 0$). In other words, there is a maximum number of particles (or maximum density) that can be accounted for with a Bose

distribution *after imposing the continuum approximation for the density of states*. This maximum number is given by

$$N_{cr} = \frac{V}{4\pi^2} \left(\frac{2mk_B T}{\hbar^2} \right)^{3/2} 1.36\pi^{1/2} = 2.612V\rho_q \quad (22)$$

where $\rho_q = \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2}$ as before. This result corresponds to a critical density

$$\rho_{cr} = 2.612\rho_q \quad (23)$$

Actually this result is physically meaningless. The problem originates from a breakdown of the continuum approximation, which cannot properly take into account the discontinuous nature of the occupation number as we approach zero energy. That there should be a problem as the energy goes to zero might have been expected from the fact that, if $E - \mu = 0$, the Bose distribution function diverges. In fact one can have a macroscopic number of particles in the ground state of the system, and this happens exactly when $\mu = 0$. As we shall see in a later chapter, this actually happens at a finite temperature – the so-called “Bose condensation temperature” – and this result is related to the phenomenon of ***Bose-Einstein condensation***, which we will treat in a chapter to come.

Finally, we remark that just as for the Fermi gas, the general finite T behavior of $\mu(T)$, obtained by solving equation (11) numerically, shows that $\mu(T)$ is identically zero for $T < T_c$, where T_c is the Bose condensation temperature; above T_c , it is negative, and the high-T limiting behavior has increasingly negative $\mu(T)$, just as for the Fermi gas. We return to this point in section 6(c).

6(b) Classical Statistics

We now come to the question of how and when a quantum gas shows classical properties. We are all familiar with classical gases – the gases in our atmosphere behave classically, even though they are made up of atoms or molecules that are either bosonic or fermionic (typically but not always bosonic). In what follows we first look at how this happens for both bosons and fermions, and we then explore some of the properties of the classical gas.

(i) Maxwell Boltzman Distribution

As discussed above, the classical limit is attained when the average occupation number is small. As we can see from the figure on the last page, this happens when $\beta(E - \mu) \gg 1$ and thus when $\exp[\beta(E - \mu)] \gg 1$, and this for both the Fermi and Bose distribution functions. In this case the two distributions converge to what is called the ***Maxwell Boltzman distribution***, given by:

$$f_{FD, BE}(E) = \frac{1}{\exp[\beta(E - \mu)] \pm 1} \approx \frac{1}{\exp[\beta(E - \mu)]} = \exp[\beta(\mu - E)] = f_{MB}(E) \quad (24)$$

In this classical limit the fermionic or bosonic nature of the particles is irrelevant since two particles are rarely in the same state – the occupation probability in a state of energy E is falling off exponentially with E as $\exp[-(E-\mu)/k_B T]$.

The chemical potential in this case can easily be evaluated. As before, we start by writing the expectation value for the total particle number, this time in terms of the canonical partition function Z_1 , as

$$N = \rho V = \sum_i f(E) \approx V \int g(E) f(E) dE = \alpha V \int_0^{\infty} g(E) \exp[-\beta E] dE = \alpha Z_1 = \alpha V \rho_q \quad (25)$$

where the “quantum density” ρ_q was defined in chapter 4 (see eqn. (4.66)). Since for a particle in 3D, we have the canonical partition function as (cf eqtns. (4.60) and (4.66)):

$$Z_1 = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\infty} E^{1/2} \exp[-\beta E] dE = V \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} = V \rho_q \quad (26)$$

it then follows that the activity is just

$$\alpha = \exp[\beta\mu] = \frac{\rho}{\rho_q} \quad \text{or} \quad \mu = k_B T \ln[\rho / \rho_q] \quad (27)$$

This is exactly the result we used in the last chapter, for the behavior of the chemical potential in a low-density gas, to treat the problem of a partially ionized gas (see eqn. (5.37)). As we have already seen, it is of great practical importance.

Note in the low density limit $\rho / \rho_q \ll 1$ (where the Maxwell-Boltzmann distribution applies) the chemical potential μ must be negative. This is easy to understand - adding a particle to an ideal gas increases the energy of the system (U) but there is an even larger increase in entropy term of the free energy (TS) leading to a net decrease in $F = U - TS$. Thus we have, in this low density limit, that

$$\mu \equiv \left(\frac{\partial F}{\partial N} \right)_V < 0 \quad (28)$$

Note that this will happen if either the density is low (so that there are many available states for any added particle), or if the temperature is high; in both cases the TS term in F is more important than the U term. At the end of this chapter we look in detail at the behavior of $\mu(T)$ for the Maxwell-Boltzmann gas.

Note that, as we have already seen, this limiting behaviour in the Maxwell-Boltzmann case is not true for the degenerate Fermi gas. This is because at low T , such that $k_B T < E_F$, the entropy of a degenerate Fermi gas is much smaller than that of a classical gas (since most states well below the Fermi energy are “locked in”). As we shall see later (and as already noted earlier), at higher T the chemical potential of a Fermi gas also becomes negative.

Consider now the energy distribution for a Maxwell-Boltzmann gas; we have

$$\begin{aligned}
 P(E)dE &= \frac{V}{Z_1} g(E) \exp[-\beta E] dE = \frac{V}{\rho_q V 4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \exp[-\beta E] dE \\
 &= \frac{1}{4\pi^2} \left(\frac{2\pi\hbar^2}{mk_B T}\right)^{3/2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \exp[-\beta E] dE = 2\pi^{-1/2} \beta^{3/2} E^{1/2} \exp[-\beta E] dE
 \end{aligned} \tag{29}$$

One can also convert this to velocity distribution using $E = mv^2/2$, so that $dE = mv dv$; we then have the more familiar Maxwell-Boltzmann velocity distribution, viz.,

$$P(v)dv = 2\pi^{-1/2} \beta^{3/2} mv \left(\frac{mv^2}{2}\right)^{1/2} \exp[-\beta mv^2/2] dv = \left(\frac{2}{\pi}\right)^{1/2} (m\beta)^{3/2} v^2 \exp[-\beta mv^2/2] dv \tag{30}$$

This result was first derived by Maxwell in the 19th century using elementary probabilistic considerations.

(ii) Free Energy & Entropy

From the results just derived, we can easily find the free energy for a Maxwell-Boltzmann gas. Let us first recall from Chapter 1 that we can define the chemical potential either as the change in energy U of the system, with S and V held constant, if we add a particle (cf. eqn. (1.50)); or the change in free energy F of the system, now with T and V held constant, if we add a particle (cf. eqn. (1.51)). Conversely, if we know how μ varies with particle number r we can determine F (we use the symbol r here for particle number since n is already being used for the distribution function).

For example, consider an ideal gas such that $\rho = \frac{r}{V} \ll \rho_q$, the quantum density, and so from (27)

$$\mu = k_B T \ln\left(\frac{\rho}{\rho_q}\right) = k_B T \ln\left(\frac{r}{V\rho_q}\right) \tag{31}$$

Where we see explicitly how the chemical potential changes with r . Now let us write the free energy as a sum over contributions for each particle, as we add the particles one by one, assuming that when we add the r -th particle we add a free energy $\mu(r)$. We then get, by summing r up to N , the result

$$F = \sum_{r=1}^N \mu(r) = k_B T \sum_{r=1}^N \ln\left(\frac{r}{V\rho_q}\right) = k_B T \sum_{r=1}^N (\ln[r] - \ln[V\rho_q]) = \frac{1}{\beta} (\ln[N!]) - N \ln[V\rho_q] \tag{32}$$

This is an interesting result – it gives us a canonical potential (not a grand canonical potential, since we have now fixed the number of particles to be N) of form

$$Z_N = \exp[-\beta F] = \frac{(\rho_q V)^N}{N!} = \frac{Z_1^N}{N!} \quad (33)$$

Now we might actually have been expecting here a result different from this – the intuitive assumption is that if we are dealing with classical particles, then they must look like a set of distinguishable particles, as in classical physics. However we see that this is wrong; the result in (33) is smaller than the partition function for N distinguishable particles, Z_N^d , by a factor of $N!$ (we have already seen this result for distinguishable particles in eqn (4.28)).

What is going on here? Actually we already know the answer to this question – we are describing the Maxwell-Boltzmann gas as a limit of a quantum gas, so we are already assuming indistinguishable particles – our classical intuition is simply no longer applicable. The classical result assumes $N!$ distinguishable states to get Z_N^d since there are $N!$ ways of arranging N distinguishable particles in N different states. However as we have seen there is only one quantum many body state that can be formed from all these single particle states. Thus, if the particles are truly indistinguishable then in using Z_N^d we have over counted the number of states by a factor of $N!$

We can say quite a lot more here. Note that in the limit of large N the free energy in eqn. (32) can be written as

$$F = \frac{1}{\beta} (\ln[N!] - N \ln[V\rho_q]) \approx \frac{1}{\beta} (N \ln[N] - N - N \ln[V\rho_q]) = Nk_B T (\ln[\rho / \rho_q] - 1) \quad (34)$$

which is a perfectly sensible looking result. On the other hand for N distinguishable particles the free energy becomes

$$F^d = -\frac{1}{\beta} N \ln[V\rho_q] = Nk_B T (\ln[\rho / N\rho_q]) = Nk_B T (\ln[\rho / \rho_q] - \ln[N]) \quad (35)$$

Now this result does **not** make sense, because we see that F^d is *not extensive*; it has a term proportional to the function $N \ln N$, whereas an extensive quantity would have to be proportional to N . On the other hand we see from (34) that the free energy F for indistinguishable particles is extensive.

That there was something wrong with the classical result was clearly recognized by Gibbs in 1876, who formulated it as a paradox – note that this was 50 yrs before quantum mechanics was discovered, and before the whole business could be cleared up properly. Thus the result (34) for the free energy caused lengthy discussion in the physics literature for a long period – indeed it is still discussed today.

Before we come to discuss Gibb's paradox formally, we first need to find the entropy of the Maxwell-Boltzmann gas. This is found by differentiating the free energy in the usual way – we get

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -Nk_B \left(\ln[\rho] - \ln[\rho_q] - 1 - T \frac{\partial \ln \rho_q}{\partial T} \right) = -Nk_B \left(\ln[\rho] - \ln[\rho_q] - 1 - \frac{T}{\rho_q} \frac{\partial \rho_q}{\partial T} \right) \\ &= -Nk_B \left(\ln[\rho] - \ln[\rho_q] - 1 - \frac{3}{2} \right) = -Nk_B \left(\ln[\rho / \rho_q] - \frac{5}{2} \right) = Nk_B \left(\ln[\rho_q / \rho] + \frac{5}{2} \right) \end{aligned} \quad (36)$$

and we note again that this result is extensive. This result called the Sackur-Tetrode equation; again, it was found before the discovery of quantum mechanics, this time in 1912. Note that it contains \hbar even though it is valid at high temperatures where quantum mechanics is typically unimportant (however, Sackur and Tetrode did have available to them the Planck and Einstein formulations of statistical mechanics, in which Planck's constant appeared, even though there was no formal theory of quantum mechanics at that time).

One can also calculate the internal energy of the Maxwell-Boltzmann gas; if we do this directly from the partition function we simply have

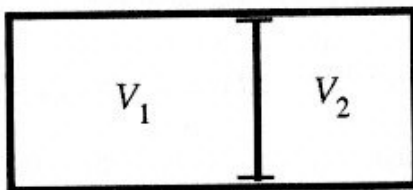
$$U = -\frac{\partial \ln[Z_1^N / N!]}{\partial \beta} = -N \frac{\partial}{\partial \beta} \left(\ln[\rho_q] - \ln[\rho] + \ln[N] + \frac{1}{N} \ln[N!] \right) = \frac{3}{2} N k_B T \quad (37)$$

Which is the same as for a gas of distinguishable particles, and does not contain Planck's constant! Thus unlike F and S , U does not depend on \hbar for an ideal gas. Why the difference? The answer is that in the classical regime, U is simply the sum over the thermal energies in each degree of freedom (the 'equipartition theorem'); but the entropy (and hence the free energy) is a more complicated quantity which depends on the way in which states are counted.

In any case, we see that QM is needed to get some of the key results for a gas, even in the high-T classical regime, and this has a profound effect on observables such as S and F even at very high temperatures.

(iii) Gibbs' Paradox

Let's now return to the Gibbs paradox. Let's consider a box at temperature T with a divider separating 2 compartments with volumes V_1 and V_2 . Initially we will assume that $V_1 = V_2$. Assume also that there are N atoms of gas made from particles of A in the volume V_1 , and N atoms of gas made from particles of type B in the volume V_2 . This is an example of a "thought experiment", designed to elicit general features of a problem.



We wish to determine the total entropy of the combined system. We can easily do this using the Sackur-Tetrode, ie., eqn (36) above. The thought experiment runs in 2 stages, viz.,

(i) We start from the initial state as shown in the Figure, with $V_1 = V_2$. Then the total entropy in this initial state is the sum of the two entropies from the gases in each compartment:

$$S_{tot}^{before} = Nk_B \left(\ln[\rho_q^A V_1 / N] + \frac{5}{2} \right) + Nk_B \left(\ln[\rho_q^B V_2 / N] + \frac{5}{2} \right) \quad (38)$$

where we define densities

$$\rho_q^A \equiv \left(\frac{m_A k_B T}{2\pi\hbar^2} \right)^{3/2} \quad \text{and} \quad \rho_q^B \equiv \left(\frac{m_B k_B T}{2\pi\hbar^2} \right)^{3/2} \quad (39)$$

(ii) Now we simply remove the divider between the compartments. Then both the A and B gases expand to a the full volume $V = 2V_1 = 2V_2$, and so the total entropy increases by an amount $2Nk_B \ln 2$. We thus have

$$S_{tot}^{after} = Nk_B \left(\ln[2\rho_q^A V_1 / N] + \frac{5}{2} \right) + Nk_B \left(\ln[2\rho_q^B V_1 / N] + \frac{5}{2} \right) = S_{tot}^{before} + 2Nk_B \ln 2 \quad (40)$$

The additional term is called the *entropy of mixing*. It is to be expected since we have increased the number of states available to both gases.

Now for the paradox. Suppose the gases A and B are truly indistinguishable – in this case, since we have the same number of particles in each compartment in the initial state, and $V_1 = V_2$, the densities are also the same in each compartment. In this case, when we remove the divider, nothing happens – the 2 gases will mix but since the pressures don't change and particles are indistinguishable, the state afterwards is the same as before. Thus the total entropy doesn't change either when the divider is removed.

If we follow the change in entropy in this case, we see first that the entropy before the divider is removed is basically the same as for when A is different than B; we have:

$$S_{tot}^{before} = Nk_B \left(\ln[\rho_q^A V_1 / N] + \frac{5}{2} \right) + Nk_B \left(\ln[\rho_q^B V_2 / N] + \frac{5}{2} \right) = 2Nk_B \left(\ln[\rho_q^A V_1 / N] + \frac{5}{2} \right) \quad (41)$$

However, unlike the case when A is different than B, if we remove the divider the total entropy remains unchanged:

$$S_{tot}^{after} = 2Nk_B \left(\ln[\rho_q^A 2V_1 / 2N] + \frac{5}{2} \right) = S_{tot}^{before} \quad (42)$$

Note the key difference between the two cases is the behaviour of the density $\rho = N/V$ inside the log function. When the particles are different the densities for each type of atom (A and B) decreases by a factor of 2 when the divider is removed. On the other hand when the particles are the same the density remains unchanged. This density term in the entropy can be traced back to the $N!$ factor in the partition function $Z_N = Z_1^N / N!$ for identical particles.

There are various ways to look at this result, and of course the discussion of it changed after QM was discovered. This was considered a paradox since one can make the atoms of type A and B more or less identical, ie., we can imagine performing a continuous limiting process in which type A tends to type B. . From a classical viewpoint the properties of the two gases would then be expected to tend to each other in a

continuous way. Nevertheless the entropy does change discontinuously when the two kinds of atom become truly identical. This result was inexplicable until the discovery of QM.

Even more troublesome for early workers in classical statistical mechanics was the fact that in classical mechanics the free energy and entropy for an ideal gas are no longer extensive. We saw this for the free energy in eqn. (35) above; and one gets the same result for the entropy of a gas calculated in classical physics, assuming distinguishable particles – one finds that

$$S^d = -\left(\frac{\partial F^d}{\partial T}\right)_{V,N} = Nk_B \left(\ln[V\rho_q] - T \frac{\partial \ln V\rho_q}{\partial T} \right) = Nk_B \left(\ln[V\rho_q] + \frac{3}{2} \right) \quad (43)$$

which is also not extensive.

We can summarize this discussion by saying that in Nature, a classical gas of identical particles is not at all what it seems. It is actually a Maxwell-Boltzmann gas whose statistical mechanics is obtained by going to the limit of small occupation number of each state – where the statistics apparently does not matter. But it still shows up in the state counting – the indistinguishability of the particles leads to the $1/N!$ factor in Z_N , as compared to a gas of distinguishable particles.

(iv) Molecules & Internal Degrees of Freedom

Up until now we have assumed that the particles in our gas are “point particles” whose only degrees of freedom are in their translational motion in 3 dimensions. However this is only true for very few gases (eg., He, or the Noble gases, or gases in outer space).

More commonly the gas particles will have internal degrees of freedom (e.g. rotation, vibration, spin). At higher energies one can also excite internal electronic degrees of freedom – thus, in ordinary H gas, one can excite to an infinite set of higher levels before the H ionizes. Even more important is the fact that almost all gases at typical terrestrial temperatures are actually molecular.

To deal with this we must add these degrees of freedom to our description. In the simplest approximation we assume that the internal degrees of freedom decouple completely from the translational degrees of freedom. In that case, we can write the total energy of the system as $E_i + E_t$, ie., the sum of the internal and translational energies.

Consider now a single fermion in which we have internal degrees of freedom. The grand partition function for a fermion in which the translational state is fixed, with energy E_t , is then given by

$$\Xi = \sum_{i,n} \exp[\beta(n\mu - (E_i + E_t))] = 1 + \alpha \sum_i \exp[-\beta(E_i + E_t)] = 1 + \alpha Z_{\text{int}} \exp[-\beta E_t] \quad (44)$$

so that the average occupation number is:

$$f_f(E_t) = \frac{\alpha}{\Xi} \left(\frac{\partial \Xi}{\partial \alpha} \right)_T = \frac{\alpha Z_{\text{int}} \exp[-\beta E_t]}{1 + \alpha Z_{\text{int}} \exp[-\beta E_t]} \approx \alpha Z_{\text{int}} \exp[-\beta E_t] \quad (45)$$

where, as always, we assume $f_f(E_t) \ll 1$ (since this is an ideal gas). To get the full partition function from this we must sum over all the translational degrees of freedom. We already know how to do this – we have our previous result that

$$Z_t = \sum_t \exp[-\beta E_t] = V \rho_q \quad (46)$$

and so it immediately follows that

$$N = \alpha Z_{\text{int}} \sum_t \exp[-\beta E_t] = \alpha Z_{\text{int}} \rho_q V \quad (47)$$

for the total number. Note that we can do exactly the same thing for bosons, where the sum over internal states gives instead

$$f_b(E_t) = \frac{\alpha}{\Xi} \left(\frac{\partial \Xi}{\partial \alpha} \right)_T = \frac{\alpha Z_{\text{int}} \exp[-\beta E_t]}{1 - \alpha Z_{\text{int}} \exp[-\beta E_t]} \approx \alpha Z_{\text{int}} \exp[-\beta E_t] \quad (48)$$

In both the bosonic and fermionic case, we can now use the result for the particle number N to get the chemical potential, in the same way as we did before; we have

$$\alpha = \frac{\rho}{\rho_q Z_{\text{int}}} \quad (49)$$

for the activity, and hence we get

$$\mu = k_B T \ln \frac{\rho}{\rho_q} - k_B T \ln Z_{\text{int}} \quad (50)$$

for the chemical potential. The result for the chemical potential (ie., for the free energy per particle) is additive, ie., the first translational term adds to the 2nd term describing the internal degrees of freedom.

In exactly the same way as before, we can sum over the chemical potential for each particle to get the free energy (cf. eqtn. (32)). This gives

$$F = \sum_{r=1}^N \mu(r) = k_B T \sum_{r=1}^N [\ln[r] - \ln[\rho_q V] - \ln Z_{\text{int}}] = k_B T [\ln N! - N \ln[\rho_q V] - N \ln Z_{\text{int}}] \quad (51)$$

And we see that all we have done here is add an internal energy term to the free energy, ie., we get the free energy as $F = F_t + F_{\text{int}}$. This is of course what we expect, since the energies are additive – the translational and internal degrees of freedom being decoupled.

Notice what this implies – that

$$Z_N = \exp\left[-\frac{F}{k_B T}\right] = \frac{(Z_t Z_{\text{int}})^N}{N!} \quad (52)$$

where again we have the $N!$ term in the denominator to account for indistinguishability. If we now calculate the energy and entropy we get

$$U = -\frac{\partial \ln Z_N}{\partial \beta} = -\frac{1}{Z_t Z_{\text{int}}} \frac{N \partial (Z_t Z_{\text{int}})}{\partial \beta} = -N \left(\frac{1}{Z_t} \frac{\partial Z_t}{\partial \beta} + \frac{1}{Z_{\text{int}}} \frac{\partial Z_{\text{int}}}{\partial \beta} \right) = N (\langle E_t \rangle + \langle E_{\text{int}} \rangle) = N \left(\frac{3}{2} k_B T + \langle E_{\text{int}} \rangle \right)$$

$$S = -\left(\frac{\partial F}{\partial T} \right)_V = -\left(\frac{\partial F_t}{\partial T} \right)_V - \left(\frac{\partial F_{\text{int}}}{\partial T} \right)_V = S_t + S_{\text{int}} \quad (53)$$

ie., the sum of the average translational and internal energies, and the sum of the entropies for translation and internal degrees of freedom, respectively.

Suppose, as an example of this, we consider a molecule with both vibrational and rotational degrees of freedom, in addition to the translational ones. We assume a basic vibrational frequency ν_0 and a rotational energy constant E_0 such that the total energy is

$$E_{\text{tot}} = \frac{1}{2m} \frac{\hbar^2}{L^2} (r^2 + s^2 + t^2) + E_0(j+1)j + h\nu_0 \left(\frac{1}{2} + n \right) \quad (54)$$

For a system inside a box of side L . The single molecule partition function is just the product of the individual partition functions, ie.,

$$Z_1 = Z_t Z_{\text{rot}} Z_{\text{vib}} \quad (55)$$

and the mean total energy per particle is just the sum of the individual mean energies, ie.,

$$\langle E_{\text{tot}} \rangle = \frac{3}{2} k_B T + \langle E_{\text{rot}} \rangle + \langle E_{\text{vib}} \rangle \quad (56)$$

with a corresponding heat capacity:

$$C_v = N \frac{3}{2} k_B + N \frac{\partial \langle E_{\text{rot}} \rangle}{\partial T} + N \frac{\partial \langle E_{\text{vib}} \rangle}{\partial T} \quad (57)$$

where the second and third terms are the heat capacities for rotation and vibration respectively.

Example: For N_2 , $h\nu_0$ is 260 meV which is much bigger than $k_B T = 25 \text{ meV}$ at 300K. On the other hand the rotational $E_0 = 0.25 \text{ meV}$ (ie., only 3K). Thus at 300K the vibrational degrees of freedom are *frozen out* and don't contribute to the entropy, energy and heat capacity, whereas the rotational degrees of freedom are already in the classical high T limit. Thus for this case we have

$$C_v \approx \frac{3}{2} N k_B + N k_B = \frac{5}{2} N k_B \quad (58)$$

On the other hand if we look at the H_2 molecule, where the moment of inertia is 14 times smaller than for N_2 , we have $E_0 \sim 50K$.

6(c) Summary – comparing Classical & Quantum Gases

In the next 2 chapters we will go into much more detail about the behavior of both Bose and Fermi gases. However it is useful here to summarize their differences. This is most easily seen if we look at the behavior of the chemical potential – we recall that this can be found by solving equation (11), ie., by fixing the number of particles to be N , and solving

$$N = \int_0^{\infty} Vg(E)f(E, \mu, T)dE = V\rho \quad (59)$$

For the chemical potential $\mu(T)$, which must vary with temperature once we have fixed N . In the discussion above I never actually did solve for $\mu(T)$, because the expressions cannot be solved analytically without a lot of work (usually one does things numerically).

The other thing that we never looked at above was the role of spatial dimension in all of this – everything was done for 3 dimensions. As a general rule the effect of thermal fluctuations is increasingly important as one lowers the number D of spatial dimensions, and the role of internal interactions is less important. Although I will not show this here, one can show that in 3 dimensions, systems almost inevitably must order, because the energy term U in the free energy always dominates over the entropy term TS as one goes to zero T . However in 2 dimensions this only happens rigorously at $T = 0$, unless there exist long-range (unscreened) forces between the elementary constituents (particles, spins, etc.) in the system (an example of this would be a two-dimensional sheet of spins, in which the long-range magnetic dipolar interactions between them allows them to order at a finite T). When we get to 1 dimension, ordering cannot happen at all – the system is always disordered.

NB: In all of these case, we suppose that the motion in one or two dimensions is simply caused by restricting the motion of 3-d particles to one or two dimensions, but that they are still behaving like bosons or fermions. Thus we are not considering 2-d anyons, or 1-d systems where statistics is undefined.

The general observations just given should be borne in mind when we look at the results for the chemical potential. We shall see, for example, that BEC in a neutral 2D Bose system can only rigorously occur for spatial dimension $D > 2$, except at $T = 0$.

Behaviour of Chemical Potential: Let us compare the chemical potential for the Bose, Fermi, and Maxwell-Boltzmann cases in the various spatial dimensions. In all cases we do this by solving (11) numerically.

To compare the 3 different cases, it is useful to define an energy scale which plays the same role in all three statistics. We will assume spinless particles in all cases. The easiest way to do this is to introduce a wave-vector k_q which is the inverse of the mean interparticle spacing, and so clearly directly related to the density of the system; we will then define an energy ε_q which is simply given by

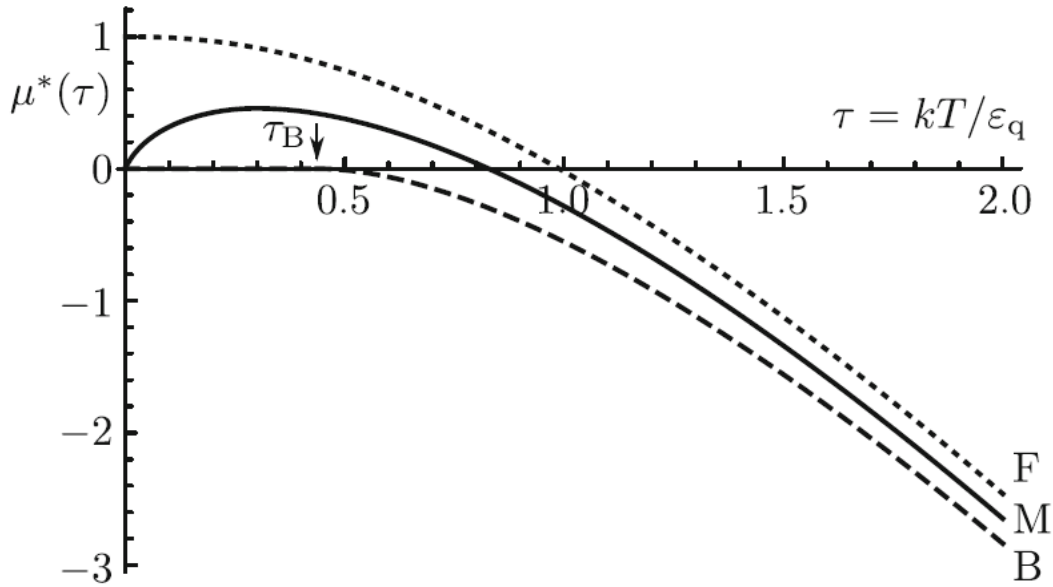
$$\varepsilon_q = (\hbar/2\pi)^2 (k_q^2/2m) \quad (60)$$

So that ε_q is simply the zero point energy associated with the confinement of a particle of mass m to a lengthscale $1/k_q$. Note that for a Fermi gas we simply have $E_F = \varepsilon_q$. Let us now turn to the results for different dimensions.

3-dimensional case: In this case the relevant length-scale is related to the mean density by

$$k_q^3 = 6\pi^2 \rho \quad (61)$$

where ρ is the particle density, ie., $\rho = N/V$. We then have: $\varepsilon_q = (\hbar/2\pi)^2 6\pi^2 \rho / 2m$ (62)



Chemical Potential $\mu^*(T) = \mu(T)/\varepsilon_q$, as a function of $\tau = k_B T/\varepsilon_q$, for: Fermi (F), Bose(B), and Maxwell-Boltzmann (M) gases, in 3 dimensions

The result of a numerical calculation is shown above. Note that as expected, all of the 3 cases have a chemical potential which becomes increasingly negative for large T . The Fermi gas starts off at $T = 0$ with $\mu(T=0) = E_F$, as we already knew – this then gradually falls so that $\mu(T \sim T_F) = 0$, and thereafter it is negative.

The Bose gas has $\mu(T) = 0$ for $T < T_c$, where $T_c / \varepsilon_q = \tau_B \sim 0.5$. The chemical potential is then negative for higher T; we note that it does not go smoothly to zero at T_c , in the that $d\mu(T)/dT > 0$ for all $T > T_c$. This immediately tells us that the specific heat must be singular at $T = T_c$.

Finally, we consider the Maxwell-Boltzmann gas. This has an interesting behaviour – it goes to zero with T, then is positive for low T before turning over to the characteristic monotonic decrease at higher T. We can actually understand the low T form of the chemical potential by going back to the standard Maxwell-Boltzmann result – recall that we have

$$\mu = k_B T \ln \left[\frac{\rho}{\rho_q} \right] \quad (63)$$

where the quantum density is

$$\rho_q \equiv \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} (2S + 1) \quad (64)$$

and where we are assuming spinless fermions here. We immediately see that we have $\mu \sim -T \ln T$, which at low T is positive, but at high T is negative. If we put all the constants back into the expression we see that $m(T)$ first becomes negative when $k_B T / \varepsilon_q \sim 0.8$. Notice also that for very high T, the ratio of the 3 distributions becomes unity, but they never actually becomes equal.

2-dimensional case: The 2-d case is actually very important in the real world – any system whose motion along the z-axis is confined to a distance less than the thermal de Broglie wavelength λ_T will behave as a 2d system in the xy-plane. There are many examples of such systems at low T, where λ_T is large; the best known is the 2d electron gas, which is of great importance in semiconductor applications. Many interesting experiments have been done on Bose systems in 2d, but this would take us too far afield.

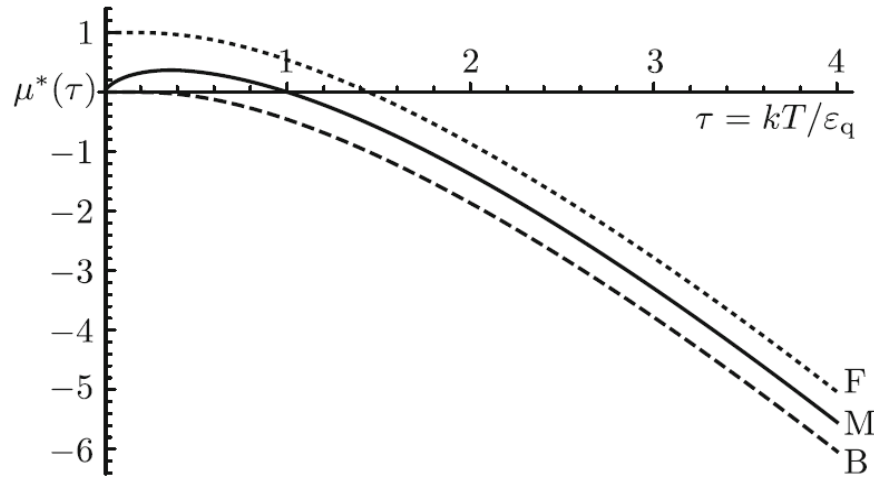
In the 2d case the relevant length-scale is now related to the mean density by

$$k_q^2 = 4\pi\rho \quad (65)$$

so that now

$$\varepsilon_q = (h/2\pi)^2 2\pi\rho/m \quad (66)$$

If we now compute the behavior of the chemical potential, we get the result shown below (next page). The most important features of these results are



Chemical Potential $\mu^*(T) = \mu(T)/\epsilon_q$, as a function of $\tau = k_B T/\epsilon_q$, for: Fermi (F), Bose(B), and Maxwell-Boltzmann (M) gases, in 2 dimensions

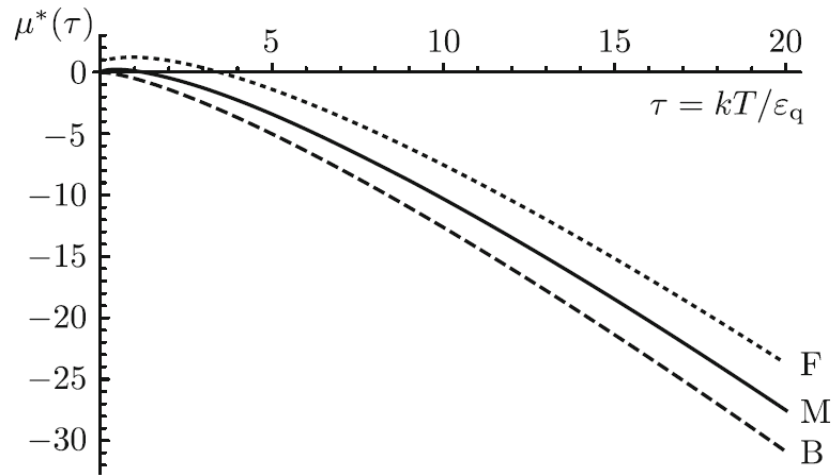
- (i) Relative to the 3d results, the chemical potential is pushed up in energy at finite T – it takes more energy to add a particle at finite T. However at T = 0 the results are identical to the 3d case.
- (ii) The chemical potential for the Bose system does not go to zero until we get to T = 0. This was already noted in the discussion above. Thus there is no finite temperature BEC in the 2d system.

Apart from these 2 features, we see that the behavior of the 2d gas is similar to that of the 3d gas; and we still have the chemical potential becoming more and more negative as we increase T. There is an interesting result, due to R May, in 2d, which is that

$$\mu^*_F - \mu^*_B = 1 \quad (67)$$

And moreover, one can show that in the limit of high T, the Maxwell-Boltzmann chemical potential μ_M lies halfway between the Fermi and Bose chemical potentials $\mu_F(T)$ and $\mu_B(T)$. Eqtn (67) simply tells us that in 2d, the separation between the Fermi and Bose chemical potentials is ϵ_q at any T.

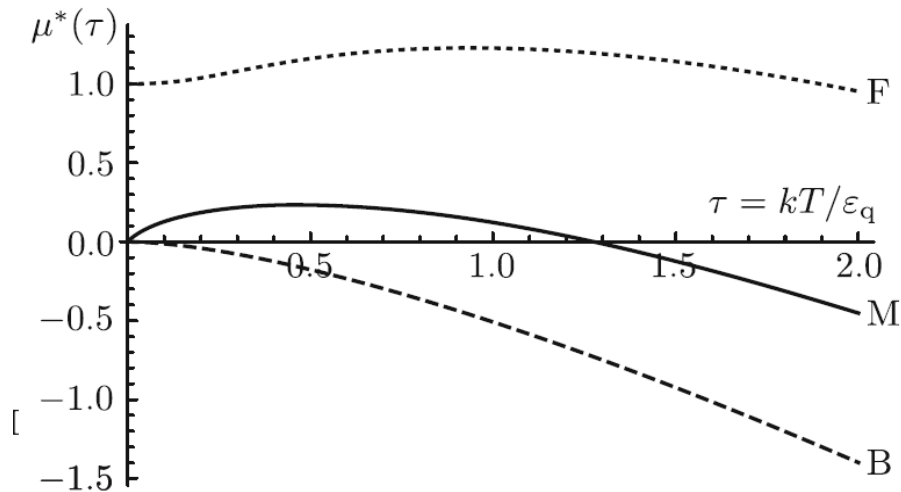
1-dimensional case: The 1-d case is also important in the real world – any system whose motion along the x- and y-axes axis is confined to lengths $< \lambda_T$ behave² as a 1d system along the z-axis. Such systems are often called “quantum wires – they include conducting chain molecules and metallic wires. The behaviour of $\mu(T)$ is as shown:



Chemical Potential $\mu^*(T) = \mu(T)/\epsilon_q$, as a function of $\tau = k_B T/\epsilon_q$, for: Fermi (F), Bose(B), and Maxwell-Boltzmann (M) gases, in 1 dimension

There are a few new features in 1 dimension; the most important of these are

- (i) Unlike in higher D, the Fermi and Bose chemical potentials actually slowly diverge from each other (and the Maxwell-Boltzmann behavior) as T gets very large (although their ratio still tends to unity in this limit).
- (ii) The Fermi chemical potential actually increases at low T, before then decreasing as before. This is not obvious in the figure above, but if we blow up the region around the origin we can see it:



Chemical Potential $\mu^*(T) = \mu(T)/\epsilon_q$, as a function of $\tau = k_B T/\epsilon_q$, for: Fermi (F), Bose(B), and Maxwell-Boltzmann (M) gases, in 1 dimension

Note that the effect of decreasing the dimension is again to push the chemical potential up, except that now the Bose chemical potential is forced away even more from the origin – it actually approaches the $T = 0$ limit quadratically in T .