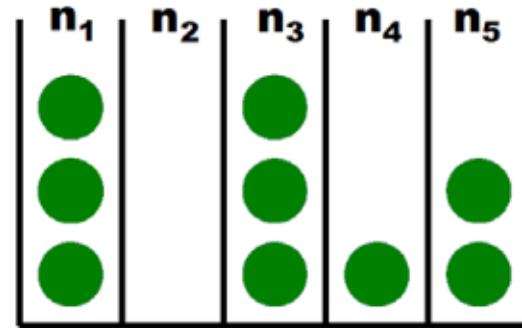
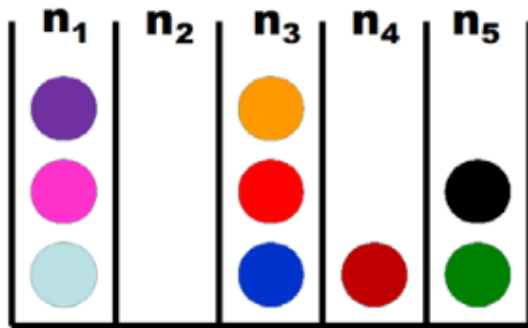


QUANTUM & CLASSICAL GASES

Recall the fundamental difference between distinguishable & indistinguishable objects in the counting of states. Compare the following two examples:



In the case shown at left, of distinguishable particles, we know that the total number of possible states which has n_j particles in the j -th state (ie., the j -th box) is

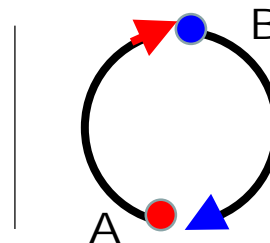
$$\Omega_{\{n_j\}}^{(N)} = C_{\{n_j\}}^N = \frac{N!}{\prod_j n_j!} \equiv \frac{N!}{n_1! n_2! \cdots n_m!} \quad (\text{distinguishable - for } N \text{ particles in } m \text{ different possible states})$$

However, if the particles are indistinguishable, we have $\Omega_{\{n_j\}}^{(N)} = 1$; the system is entirely specified by the occupation numbers $\{n_j\}$.

QUANTUM MECHANICS: Recall that in quantum mechanics in 3 dimensions we have 2 possible statistics. If we exchange a pair of identical particles we have

$$\Psi^+ = \frac{1}{\sqrt{2}} [\Psi_A(1)\Psi_B(2) + \Psi_A(2)\Psi_B(1)] \quad \text{bosons}$$

$$\Psi^- = \frac{1}{\sqrt{2}} [\Psi_A(1)\Psi_B(2) - \Psi_A(2)\Psi_B(1)] \quad \text{fermions}$$



Because the particles are identical, QM sums over the different possibilities, with +ve or -ve relative sign

1-PARTICLE DISTRIBUTION: This is the probability distribution over all states, for a single particle, in a system of N particles. We write:

$$f(\alpha) = \langle n(\alpha) \rangle \quad \text{distribution over states} \qquad f(E) \equiv \langle n(E) \rangle \quad \text{distribution over energies}$$

where $n(\alpha)$ and $n(E)$ are 1-particle occupancies, as on previous slide. A key point: since the system is entirely specified by the occupation of each state, probability distributions are now over states, not over individual particles.

FERMION STATISTICS (IDEAL GAS)

Since fermion states can only be empty or full, we have, for a single state, that

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

If there are many different states available to a system of many particles, we then just have

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

Then the 1-particle mean occupancy for a Fermi gas is

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

so that finally we have

$$f(E) = \frac{1}{1 + \exp[\beta(E - \mu)]}$$

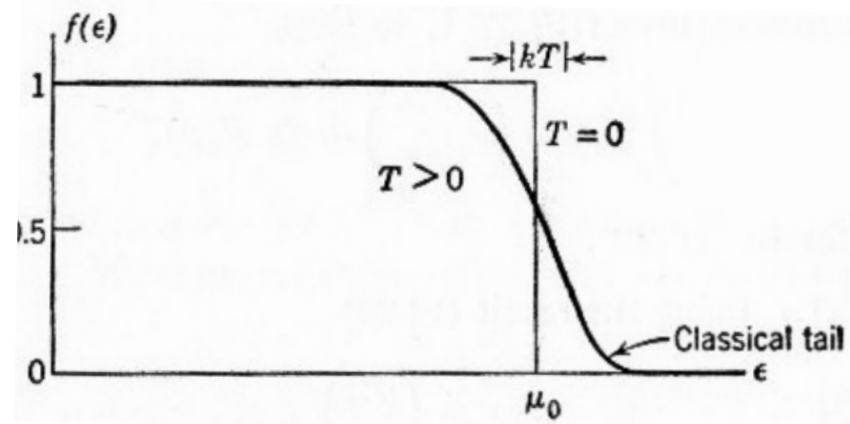
This is the "Fermi-Dirac" or "Fermi" distribution function. It gives, for fermions the probability that a state of energy E will be occupied

PROPERTIES of FERMI GAS

The Fermi distribution is shown at right for finite T ; when $T=0$, it is just a step function, with all states occupied below the chemical potential occupied.

Suppose we have a gas (no interactions), and we fix the number of particles to be N (we will relax this assumption later), with

number density $\rho = N/V$. We also define the "Fermi energy" as $E_F = \mu(T=0)$; the chemical potential itself will be a function of T and N .



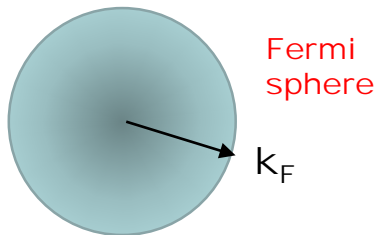
Now we know in general that
$$N = \int_0^{\infty} Vg(E)f(E, \mu, T)dE = V\rho$$

where $g(E)$ is the 1-particle density of states. Let's go to $T=0$. Then we simply have

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

But this is simply an equation that allows us to determine E_F , the $T=0$ chemical potential. Let's calculate it. We have

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



Hence: $E_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3}$, also written as $E_F = (\hbar k_F)^2 / 2m = \frac{1}{2} m v_F^2$ and as $E_F = k_B T_F$

We call T_F the Fermi temperature, and v_F the Fermi velocity

BOSON STATISTICS (IDEAL GAS)

The occupation of a boson state can be arbitrary, so now $\Xi = \sum_{n=0}^{\infty} \exp[\beta(n\mu - E(n))]$

The particles are independent, so $E(n) = nE$, where E is the single-particle energy; & thus for a gas we have

$$\Xi = \sum_{n=0}^{\infty} \exp[\beta(n\mu - nE)] = \sum_{n=0}^{\infty} (\exp[\beta(\mu - E)])^n \quad \text{which gives} \quad \Xi = \frac{1}{1 - \exp[\beta(\mu - E)]}$$

Writing this for a state α , we have $\Xi_{\alpha}(\beta, \mu) = (1 - \exp[\beta(\mu - E_{\alpha})])^{-1}$

Taking now the product over states, we find the partition function to be

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

Now we can calculate the boson occupation $\langle n(E) \rangle$ for states of different E ; we have

$$f(E) = \langle n \rangle = \beta^{-1} \Xi^{-1} \left(\frac{\partial \Xi}{\partial \mu} \right)_T \rightarrow \beta^{-1} \Xi^{-1} (-\Xi^2) (-\beta \exp[\beta(\mu - E)]) = \frac{\exp[\beta(\mu - E)]}{1 - \exp[\beta(\mu - E)]}$$

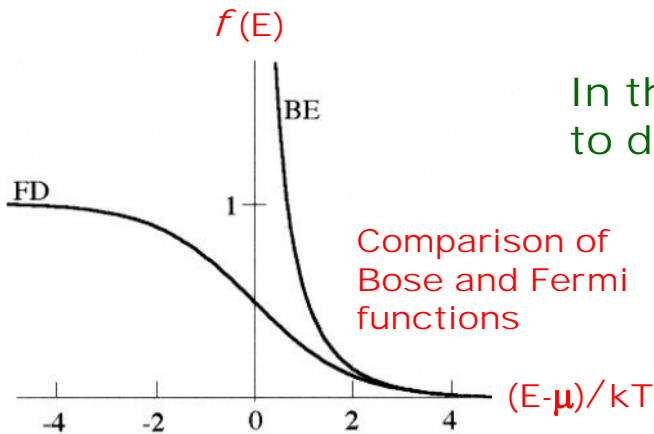
which is the same as $f(E) = \frac{1}{\exp[-\beta\mu] \exp[\beta E] - 1} = \frac{1}{\alpha^{-1} \exp[\beta E] - 1}$

In the literature one often writes $f(E) = n(E)$ for bosons, to distinguish from $f(E)$ for fermions. So finally we have

$$n(E) = \frac{1}{e^{\beta(E-\mu)} - 1}$$

Bose distribution function

This function is only defined for $E > \mu$, and diverges when $E = \mu$



BOSE GAS of MASSIVE PARTICLES: We ignore here the case of massless bosons like photons or acoustic phonons (to be discussed later).

Suppose we fix the ground state energy to define zero energy. Then the chemical potential must satisfy $\mu \leq 0$, since otherwise the Bose function is undefined. Physically, if $\mu > 0$ then the system could lower its energy without limit by continuing to populate states with energy $E < \mu$ (always possible for bosons).

Let's find the chemical potential. In the same way as for fermions, we write

$$N \approx V \int_0^{\infty} \frac{g(E)}{\exp[\beta(E - \mu)] - 1} dE \quad \text{where again} \quad g(E) = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} \quad \text{3d density of states}$$

A simple change of variables then gives

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

Now this integral has a maximum value $\sim 1.36 \pi^{1/2}$, when $\mu = 0$. But this implies that N cannot exceed a maximum value $N = N_{cr}$, given by

$$N_{cr} = \frac{V}{4\pi^2} \left(\frac{2mk_B T}{\hbar^2} \right)^{3/2} 1.36\pi^{1/2} \quad \text{corresponding to a critical density} \quad \rho_{cr} = 2.612\rho_q$$

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

It turns out that this result is **WRONG**. Physically it makes no sense - these are bosons, and so in principle one can have an arbitrarily large number of them. The problem is mathematical - we made a continuum approximation for the sum over states, and this does not work for bosons. We will fix it when we come to discuss superfluids.

CLASSICAL MAXWELL-BOLTZMANN STATISTICS (IDEAL GAS)

Suppose we assume that $\beta(E - \mu) \gg 1$, so that $\exp[\beta(E - \mu)] \gg 1$. Then it is clear that bosons and fermions will behave the same, because then

$$\frac{1}{\exp[\beta(E - \mu)] \pm 1} \rightarrow \frac{1}{\exp[\beta(E - \mu)]} = \exp[\beta(\mu - E)]$$

We then have the Maxwell-Boltzmann (MB) distribution $f_{MB}(E) = \exp[\beta(\mu - E)]$

Note that it is obtained when the occupation number is very low – this happens at high energy (ie., $(E - \mu) \gg kT$) or for low density (ie., $\rho \ll \rho_q$).

Now, yet again, let's go through the routine of finding N in terms of μ (and vice-versa). Again we have

$$N = \rho V = \sum_i f(E) \rightarrow V \int g(E) f(E) dE$$

Using the MB distribution $f_{MB}(E)$ we get $N = \rho V = \alpha V \int_0^{\infty} g(E) \exp[-\beta E] dE = : \alpha Z_1$

where Z_1 is the 1-particle canonical partition function found earlier, given by

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

Thus we find that $N = \alpha V \rho_q$ so that $\alpha = \exp[\beta\mu] = \frac{\rho}{\rho_q}$

which gives our key result

$\mu = k_B T \ln[\rho / \rho_q]$

(again!)

PROPERTIES of MAXWELL-BOLTZMANN GAS

ENERGY & VELOCITY DISTRIBUTION: The probability for a particle to have energy E is just

$$P(E)dE = \frac{V}{Z_1} g(E) \exp[-\beta E] dE \quad \rightarrow \quad \frac{V}{\rho_q V 4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \exp[-\beta E] dE$$

Multiplying out:

$$P(E)dE = \frac{1}{4\pi^2} \left(\frac{2\pi\hbar^2}{mk_B T}\right)^{3/2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \exp[-\beta E] dE = 2\pi^{-1/2} \beta^{3/2} E^{1/2} \exp[-\beta E] dE$$

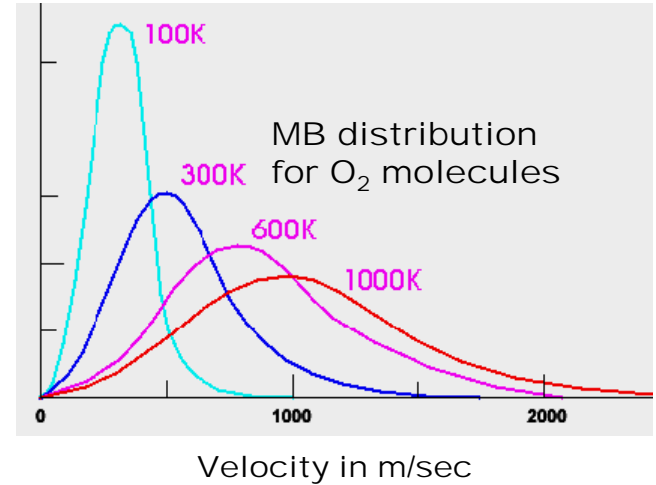
Changing variables to velocity v , we have $dE = mv dv$; so that

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

Maxwell (1860)

NB: In class we saw some animations:

<https://puu.sh/HmtLV/2c96a1d754.mp4> and <https://puu.sh/HmtSH/ae3cdd0cd1.png>



FREE ENERGY: Let's imagine adding particles to the system one by one. After adding r particles we have

Noting that $\mu \equiv \left(\frac{\partial F}{\partial N}\right)_{V,T}$ $\rho = \frac{r}{V} \ll \rho_q$ so that $\mu = k_B T \ln\left(\frac{\rho}{\rho_q}\right) = k_B T \ln\left(\frac{r}{V\rho_q}\right)$

we can then write

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

Stirling's approx. gives $F \sim \frac{1}{\beta} (N \ln[N] - N - N \ln[V\rho_q]) \rightarrow \boxed{F \sim Nk_B T (\ln[\rho / \rho_q] - 1)}$

This is a key result:

$$F \sim Nk_B T (\ln[\rho / \rho_q] - 1) \quad \text{so that} \quad Z_N = \exp[-\beta F] = \frac{(\rho_q V)^N}{N!} = \frac{Z_1^N}{N!}$$

However it is also a very puzzling result. Let's recall that for a gas of distinguishable particles, we found that

$$Z_N = Z_1^N \quad (\text{distinguishable particles})$$

This differs by the factor $N!$, and implies that for distinguishable particles

$$F^d = -\frac{1}{\beta} N \ln[V \rho_q] = Nk_B T (\ln[\rho / N \rho_q]) \quad \text{ie., we have} \quad F^d = Nk_B T (\ln[\rho / \rho_q] - \ln[N])$$

So why is the classical MB gas not the same as a gas of distinguishable particles? Let's start on this question by looking at the Free energy $F = U - TS$. For the MB gas:

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

$$\text{However } S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -Nk_B \left(\ln[\rho] - \ln[\rho_q] - 1 - T \frac{\partial \ln \rho_q}{\partial T} \right) = -Nk_B \left(\ln[\rho] - \ln[\rho_q] - 1 - \frac{T}{\rho_q} \frac{\partial \rho_q}{\partial T} \right)$$

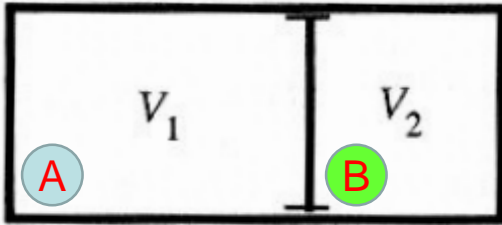
$$\text{ie., } S = -Nk_B \left(\ln[\rho] - \ln[\rho_q] - 1 - \frac{3}{2} \right) = -Nk_B \left(\ln[\rho / \rho_q] - \frac{5}{2} \right) = Nk_B \left(\ln[\rho_q / \rho] + \frac{5}{2} \right)$$

Let's note 2 things here:

- (i) both of these quantities are extensive, as they should be
- (ii) However although the energy U is truly classical (it does not depend on Planck's constant h), the entropy is not - it depends explicitly on h , through its dependence on ρ_q . How can this be?

The paradox was finally resolved by Gibbs - see next slide

GIBBS'S PARADOX & ITS RESOLUTION



Gibbs defined the following thought experiment.

(i) put gases of different particles **A** and **B** in the 2 compartments.

(ii) Now remove the partition

Recall the animation of this: <https://puu.sh/HmtLV/2c96a1d754.mp4>

The question is - for a MB gas, what is the total entropy before & after mixing?

(i) Before mixing: we have
$$S_{tot}^{before} = Nk_B \left(\ln[\rho_q^A V_1 / N] + \frac{5}{2} \right) + Nk_B \left(\ln[\rho_q^B V_2 / N] + \frac{5}{2} \right)$$
 where $\rho_q^A \equiv \left(\frac{m_A k_B T}{2\pi\hbar^2} \right)^{3/2}$ and $\rho_q^B \equiv \left(\frac{m_B k_B T}{2\pi\hbar^2} \right)^{3/2}$

(ii) After mixing: we have

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

Entropy of mixing

Now suppose particles A and B are identical...

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

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

So nothing changes in this latter case. This is problematic for several reasons...

Problems raised by Gibbs Result: This result has given rise to discussion ever since Gibbs formulated it. Here are 2 key points one can make:

(i) The limit as $B \rightarrow A$: Suppose we let B become identical to A in a continuous way. This is a process which is easily definable classically – for example, we could simply let the particles have different masses m_A and m_B , then let one tend to the other.

However, we see that in the case of the MB gas, this limit is discontinuous – the final entropy is completely different from the initial entropy, unless the particles are identical. This makes no sense classically.

(ii) Inherent inconsistency of distinguishable particle result: much more serious, and harder to absorb, is the fact that the result for a gas of classical distinguishable particles, apparently quite innocuous, is actually internally inconsistent. We note that for this system:

$$F^d = Nk_B T (\ln[\rho / \rho_q] - \ln[N]) \quad (\text{as found before})$$

& so we have

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

However neither of these results is extensive. The free energy has the factor $N \ln N$ in it, and the entropy has the factor $N \ln V$; thus neither is consistent with basic thermodynamics.