Thermal Physics - PH441 **John Waczak**
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Fermions and Bosons

We found the Fermi-Dirac distribution to be

$$f_{FD}(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}$$

and the Bose-Einstein distribution was:

$$f_{BE}(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} - 1}$$

The confusing thing here is we have energy, chemical potential, and temperature hanging out here. So how can we remember the difference between these two equations? Let's look at the energy that is exactly equal to the chemical potential. Then $f_{FD}(\mu) = \frac{1}{2}$ and $f_{BE}(\mu) = \frac{1}{0} = \infty$. And thus we see the difference between the fermions (which cant have multiple occupancy).

Classical Ideal Gas

We keep coming back to this because (a) it's something we can solve and (b) in the dilute limit this describes things pretty well (chemistry).

So the **Classical-limit** for a gas is *low density.* This means that the occupancy of any orbital will be very, very small (there's just not a lot of gas to occupy states). This tells us that $\epsilon \gg \mu$ in the classical limit. This is identical to $f(\epsilon) \ll 1$. And thus:

$$f_{\text{classical}}(\epsilon) = e^{-\beta(\epsilon-\mu)}$$

Now we want to know what the average number of particles is for this limit.

$$\begin{aligned}
\langle N_i \rangle &= \sum_i^{\text{orbitals}} f(\epsilon_i) \\
&= \sum_i^{\text{classical orbitals}} e^{-\beta(\epsilon_i - \mu)} \\
&= e^{\beta\mu} \sum_i^{\text{orbitals}} e^{-\beta\epsilon_i} \\
Z_1 &\equiv \sum_i^{\text{orbitals}} e^{-\beta\epsilon_i} = n_Q V \\
\text{where: } n_Q &= \Big(\frac{mkT}{2\pi\hbar^2}\Big)^{3/2} \text{ for one particle in a box} \\
\Rightarrow N &= \langle N_i \rangle = e^{\beta\mu} n_Q V \\
\text{thus } \frac{n}{n_Q} &= e^{\beta\mu} \\
\Rightarrow \mu &= kT \ln(\frac{n}{n_Q}) \\
&= kT\Big[\ln(N) - \ln(V) - \frac{3}{2}\ln(T) + ...\Big]
\end{aligned}$$

Now let's figure out what the free energy is. Recall that:

$$dF = -SdT - pdV + \mu dN$$

and so by holding appropriate things constant (temp,volume) then we have that:

$$\begin{aligned}
F &= \int_0^N \mu dN \\
&= kT\Big(\int_0^N \ln(N)dN + N\ln(1/Vn_Q)\Big) \\
&= kT\Big(N\ln N - N + N\ln(1/Vn_Q)\Big) \\
&= NkT\Big[\ln\Big(\frac{n}{n_Q}\Big) - 1\Big] \\
&= NkT\Big[\ln(n) + \frac{3}{2}\ln(2\pi\hbar^2) - \frac{3}{2}\ln(m) - \frac{3}{2}\ln(k) - \frac{3}{2}\ln(T)\Big] - NkT \\
S &= -\Big(\frac{\partial F}{\partial T}\Big)_{V,N} = \frac{3}{2}Nk - Nk\Big[\ln(n/n_Q) - 1\Big] \\
p &= -\Big(\frac{\partial F}{\partial V}\Big)_{T,N} = \frac{NkT}{V} \\
U &= U - TS = \frac{3}{2}NkT
\end{aligned}$$