11/28 Lecture outline

- Now let's instead maximize the correct quantum counts of microstates

$$\omega(\{N_i\})_{B.E.} = \prod_i \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!} \qquad \text{bosons}$$

$$\omega(\{N_i\})_{F.D.} = \prod_i \frac{g_i!}{N_i!(g_i - N_i)!} \qquad \text{fermions.}$$

- Bose Einstein case:

$$\ln \omega_{B.E.} \approx \sum_i [(N_i + g_i - 1)\ln(N_i + g_i - 1) - N_i \ln N_i - (g_i - 1)\ln(g_i - 1)],$$

where we used Stirling's approximation. With the Lagrange multipliers to enforce $N = \sum_i N_i$ and $U = \sum_i N_i \epsilon_i$, as in last lecture, we find

$$\ln(N_i + g_i - 1) - \ln N_i + \alpha + \beta\epsilon_i = 0.$$

which gives

$$N_i^* = (g_i - 1)\frac{1}{e^{-\alpha-\beta\epsilon_i} - 1} \approx g_i \frac{1}{e^{-\alpha-\beta\epsilon_i} - 1},$$

where we took $g_i \gg 1$ for the last step. The above result differs from M.B. thanks to the $-1$ in the denominator. We also get

$$\ln \omega_{B.E.}(\{N_i^*\}) = \sum_i [N_i^* \ln((N_i^* + g_i - 1)/N_i^*) + (g_i - 1)\ln(((N_i^* + g_i - 1)/(g_i - 1))]$$

$$= -k\alpha N - k\beta U - k\sum_i g_i \ln(1 - e^{\alpha+\beta\epsilon_i})$$

And now comparing with $S = \frac{1}{T}U + \frac{PV}{T} - \frac{1}{T}\mu N$ we have $\alpha = \mu/kT$ and $\beta = -1/kT$, as before, but now the equation of state is

$$PV = -kT\sum_i g_i \ln(1 - e^{\alpha+\beta\epsilon_i}).$$

And $S = k\ln\omega_{max}$, without the need to put in by hand the $1/N!$ as in the MB case.

- Fermi Dirac case:

$$\ln \omega_{F.D.} \approx \sum_i [g_i \ln g_i - N_i \ln N_i - (g_i - N_i)\ln(g_i - N_i)],$$

This is maximized for

$$\ln((g_i - N_i)/N_1) + \alpha + \beta\epsilon_i = 0,$$

which gives

$$N_i^* = g_i \frac{1}{e^{-\alpha-\beta\epsilon_i} + 1}.$$

Note that this properly satisfies $N_i^* \leq g_i$. Again, $\alpha = \mu/kT$, and $\beta = -1/kT$ and $S \approx k \ln \omega_{max}$, and now

$$PV = kT \sum_i g_i \ln(1 + e^{\alpha+\beta\epsilon_i}).$$

- Summarize,

$$\frac{N_i^*}{g_i} = \frac{1}{e^{-\alpha-\beta\epsilon_i} + a}$$

with $a = -1$ for Bose case (integer spin, e.g. photons), $a = +1$ for Fermi case (odd half-integer spin, e.g. electrons), and $a = 0$ for the M.B. case. Plot this as a function of $x = (\epsilon_i - \mu)/kT$. These cases all agree in the classical limit, which is where $x \gg 1$ i.e. where

$$e^{-\alpha-\beta\epsilon_i} \gg 1$$

, i.e. when

$$N_i^*/g_i \ll 1.$$

Since $N_i^*/g_i = (N/Z)e^{-\epsilon_i/kT}$, the system behaves classically if

$$N \ll Z$$

Which for a monatomic gas becomes

$$\frac{h}{\sqrt{2\pi mkT}} \ll \left(\frac{V}{N}\right)^{1/3}.$$

In words: the thermal wavelength (LHS) should be small compared to the inter-particle distance.

In the classical limit $\mu = kT \ln(N/Z)$ is very negative. Decreasing $T$ then decreases $x$, and eventually the physics of the MB, BE, FD distinction becomes important. Note that in the classical limit, all the above equations of state simply reduce to the ideal gas law, $PV = NkT$.

- BE case: $\mu \to 0$ at finite $T$, and then $N_i^*$ diverges for $\epsilon_i = 0$. This is Bose condensation.

• FD case: at low temperature, $\mu$ becomes positive, so that $N_i^* \cong 1$ for $\epsilon_i < \mu$ and zero for $\epsilon_i > \mu$. This has important consequences. It's called the Fermi-liquid theory of low-temperature metals.

• New topic: system of harmonic oscillators, in equilibrium at temperature $T$. Take each H.O. to be non-interacting with the rest, so can study single H.O.. Take them to be distinguishable, so can use M.B. statistics. 3d H.O. is the sum of 3 1d H.O.s. For 1d H.O., we have $\epsilon = p^2/2m + \frac{1}{2}m\omega^2x^2$. Partition function:

$$Z = \int \frac{dpdx}{h} e^{-p^2/2mkT} e^{-m\omega^2x^2/2kT} = h^{-1}\sqrt{2\pi mkT}\sqrt{2\pi kT/m\omega^2} = \frac{kT}{h\nu},$$

where $\omega = 2\pi\nu$. Then

$$\overline{\epsilon} = kT^2 \frac{\partial}{\partial T} \ln Z = kT,$$

which is the classical equi-partition of energy, accounting for $\overline{K.E.} = \overline{P.E} = \frac{1}{2}\overline{\epsilon}$. In this case, for 3d H.O.s, $U = 3NkT$ and $C_V = 3Nk$, twice that of monatomic ideal gas.

Now instead use Q.M. energies of H.O.: $\epsilon_n = (n + \frac{1}{2})h\nu$. Compute

$$Z = \sum_{n=0}^{\infty} e^{-\epsilon_n/kT} = e^{-h\nu/2kT} \sum_{n=0}^{\infty} (e^{-h\nu/kT})^n = e^{-h\nu/2kT} \frac{1}{1 - e^{-h\nu/kT}}.$$

where we used $g_n = 1$, and summed the geometric series. For high temperature, this gives $Z \approx kT/h\nu$, which agrees with the approximate answer above. The energy is

$$U = 3NkT^2 \frac{\partial}{\partial T} \ln Z = 3N \left[ \tfrac{1}{2}h\nu + \frac{h\nu}{e^{h\nu/kT} - 1} \right].$$

For $T \to 0$, this gives $U \to 3N(\frac{1}{2}h\nu)$, all the H.O.s are in their groundstate. For high temperature, $kT \gg h\nu$, on the other hand, we expand the above to get $U \approx 3N(\frac{1}{2}h\nu + kT - \frac{1}{2}h\nu) = 3NkT$, which is the classical equipartition answer.