12/4 Lecture outline

• Recall

$$S(U, N, ...) = k \ln \Omega(U, N, ...) \approx k \ln \omega_{max}.$$

$$\Omega(U, N) = \sum_{\{N_i\}}{}' \omega(\{N_i\}),$$

where the prime is a reminder that the $\{N_i\}$ must satisfy $\sum_i N_i = N$ and $\sum_i N_i \epsilon_i = U$. Can work out what S this gives for for the different cases:

$$\omega_{M.B.}(\{N_i\}) = N! \prod_{i=1}^{n} \frac{g_i^{N_i}}{N_i!},$$

$$\omega_{M.B.G.}(\{N_i\}) = \prod_{i=1}^{n} \frac{g_i^{N_i}}{N_i!},$$

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

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

• Work it out for the M.B.G. distribution. Maximize it over microstates, subject to the constraints that we reproduce the macroscopic U and N. Using Stirling's approximation (taking all N_i large) we have

$$\ln \omega_{M.B.}(\{N_i\}) = \sum_{i=1}^{n} N_i \ln g_i - \ln N_i! \approx \sum_i N_i \left[\ln \left(\frac{g_i}{N_i} \right) + 1 \right].$$

We want to maximize this, over all N_i, subject to the constraints $N = \sum_i N_i$ and $U = \sum_i N_i \epsilon_i$. Use Lagrange mulipliers to enforce these constraints. So maximize

$$\sum_i N_i \left[\ln \left(\frac{g_i}{N_i} \right) + 1 + \alpha + \beta \epsilon \right],$$

over all N_i, where α and β are Lagrange multipliers. Get that ω is maximized for $N_i = N_i^*$, given by

$$N_i^* = g_i \exp(\alpha + \beta \epsilon_i),$$

$$\ln \omega_{max} \approx -\alpha N - \beta U + N.$$

Recall from thermodynamics that

$$U - TS + PV \equiv G = \mu N,$$

so

$$S = -\frac{\mu}{T}N + \frac{1}{T}U + \frac{PV}{T}$$

Compare with

$$k \ln \omega_{max} \approx k\alpha N - k\beta U + kN.$$

Fits with

$$PV = NkT$$

$$\alpha = \mu/kT$$

$$\beta = -1/kT$$

- Summary: Find ω_{MBG} is maximized, for fixed U and N, by taking

$$N_i^* = g_i \exp(\alpha + \beta\epsilon_i),$$

$$\alpha = \mu/kT$$

$$\beta = -1/kT$$

where we still need to enforce

$$N = \sum_i N_i^* = e^\alpha \sum_i g_i e^{\beta\epsilon_i}$$

$$U = \sum_i N_i^* \epsilon_i = e^\alpha \sum_i g_i \epsilon_i e^{\beta\epsilon_i}.$$

This gives

$$S = k \ln \Omega \approx k \ln \omega_{max} \approx -k\alpha N - k\beta U + kN.$$

Compare with

$$S = -\frac{\mu}{T}N + \frac{1}{T}U + \frac{PV}{T},$$

to get the above identifications of α and β, and also $PV = NkT$; this shows that the k appearing in $S = k \ln \Omega$ is the same k constant as appears in the ideal gas law.

- Define the partition function (of single molecule)

$$Z(T, V) \equiv \sum_i g_i e^{\beta\epsilon_i},$$

Then $e^\alpha = N/Z$ and so the chemical potential per molecule is

$$\mu = kT \ln(N/Z).$$

Also, $U = N(\frac{\partial}{\partial\beta}\ln Z)_{\epsilon_i}$ which can be written as

$$U = NkT^2\left(\frac{\partial}{\partial T}\ln Z\right)_V.$$

Then

$$S = \frac{U}{T} + \frac{PV}{T} - \frac{\mu N}{T} = \frac{U}{T} + Nk + Nk\ln(Z/N),$$

$$F = U - TS = -NkT\left(1 + \ln(Z/N)\right).$$

$$G = N\mu = NkT\ln(N/Z).$$

- Example of ideal monatomic gas.

$$Z = \sum_i g_i e^{\beta\epsilon_i} \approx \int_0^\infty e^{\beta\epsilon} g(\epsilon)d\epsilon$$

$$= \int_0^\infty e^{-\epsilon/kT}\left(\frac{4\sqrt{2}\pi V}{h^3}m^{3/2}\epsilon^{1/2}\right)d\epsilon$$

$$= V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}.$$

So then

$$\mu = kT\ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right],$$

$$U = NkT^2(\frac{3}{2}\frac{1}{T}) = \frac{3}{2}NkT,$$

$$S = NK\left[\frac{5}{2} + \ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]\right],$$

$$F = -NkT\left[1 + \ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]\right].$$

Verify: $S = -(\partial F/\partial T)_{V,N}$ and $P = -(\partial F/\partial V)_{T,N}$.

- Molecular speed distribution. $N(\epsilon)d\epsilon = e^{\alpha+\beta\epsilon}g(\epsilon)d\epsilon$. So

$$p(\epsilon)d\epsilon = \frac{N(\epsilon)d\epsilon}{N} = \frac{g(\epsilon)e^{\alpha+\beta\epsilon}d\epsilon}{\int_0^\infty e^{\alpha+\beta\epsilon}g(\epsilon)d\epsilon},$$

$$= \frac{2}{\sqrt{\pi}(kT)^{3/2}}e^{-\epsilon/kT}\epsilon^{1/2}d\epsilon,$$

where we used $g(\epsilon) \sim \sqrt{\epsilon}$ (which follows from $g(\epsilon)d\epsilon = \frac{1}{8}4\pi n^2 dn$ and $\epsilon = \hbar^2\pi^2 n^2/2mL^2$). Using $\epsilon = \frac{1}{2}mv^2$, this agrees with the Maxwell velocity distribution. Also, the average energy per particle is

$$\bar{\epsilon} = \int \epsilon p(\epsilon) d\epsilon = U/N = \frac{3}{2}kT,$$

which is the equipartition of energy for a monatomic molecule.

• The MBG approximation is valid in the classical regime; this is the case if the gas is dilute, meaning that we require $N_i \ll g_i$. Example in book: Helium gas at STP, find $N_i/g_i \approx 4 \times 10^{-6}$, so indeed in classical regime.

• Now let's instead maximize the 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 above, 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:

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

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 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, μ 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.