

11/21 Lecture outline

- Last time. Find ω_{MB} 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

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

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

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

- Example of ideal monatomic gas.

$$\begin{aligned} Z &= \sum_i g_i e^{\beta \epsilon_i} \approx \int_0^\infty e^{\beta \epsilon} g(\epsilon) d\epsilon \\ &= \int_0^\infty e^{-\epsilon/kT} \left(\frac{4\sqrt{2}\pi V}{h^3} m^{3/2} \epsilon^{1/2} \right) d\epsilon \\ &= V \left(\frac{2\pi mkT}{h^2} \right)^{3/2}. \end{aligned}$$

So then

$$\begin{aligned} \mu &= kT \ln \left[\frac{N}{V} \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \right], \\ U &= NkT^2 \left(\frac{3}{2} \frac{1}{T} \right) = \frac{3}{2} NkT, \\ S &= NK \left[\frac{5}{2} + \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] \right], \\ F &= -NkT \left[1 + \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] \right]. \end{aligned}$$

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

$$\begin{aligned} p(\epsilon)d\epsilon &= \frac{N(\epsilon)d\epsilon}{N} = \frac{g(\epsilon)e^{\alpha+\beta\epsilon}d\epsilon}{\int_0^\infty e^{\alpha+\beta\epsilon}g(\epsilon)d\epsilon}, \\ &= \frac{2}{\sqrt{\pi}(kT)^{3/2}} e^{-\epsilon/kT} \epsilon^{1/2} d\epsilon, \end{aligned}$$

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 MB 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.