12/6 Lecture outline

- 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,

$$\frac{N_i^*}{g_i} = \frac{1}{e^{(\epsilon_i-\mu)/kT} + a}$$

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.

• Einstein's model for the specific heat of solids. Model a solid with N atoms as N 3d harmonic oscillators, with some frequency ω_E. This is equivalent to $3N$ 1d harmonic oscillators, since $H_{3d} = \vec{p}^2/2m + \frac{1}{2}m\omega^2\vec{x}^2 = H_x + H_y + H_z$. Note: the 3N oscillators are effectively distinguishable, since at different locations, so can use ω_{MB}. But we also describe the excitations of the harmonic oscillator in terms of *phonons*, which behave like indistinguishable bosons. These energy excitations are not real particles, in any classical sense, but the quanta of vibrations behave particle-like, so they're called quasiparticles.

• Compute the partition function Z of a 1d harmonic oscillator.

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

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.

• Einstein theory for C of solid. N atoms $\approx 3N$ distinguishable 1d SHOs.

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

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3Nk(\theta_E/T)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2},$$

with $\theta_E \equiv h\nu/k$. For $T \gg \theta_E$, get $C_V \approx 3Nk$. For $T \ll \theta_E$, get $C_V \approx 3Nk(\theta_E/T)^2 e^{-\theta_E/T}$. When θ_E/T is small, we have the equipartition expression, including the vibrational d.o.f.. When θ_E/T is large, the vibrational d.o.f. is not excited – the atom is in the groundstate. Note that $\theta_E \sim \nu \sim \sqrt{\kappa/\mu}$ is large for light elements or those that are very stiff, e.g. for diamond $\theta_E = 1450K$. A single curve gives a very good approximation for $C_V(T)$, for different solids (measurement at one value of T suffices to determine θ_E) and temperatures. However, discrepancies for range $T \sim \theta_E$ and below.

• This topic was only briefly mentioned in lecture: Debye's improvement to Einstein's model. Replace atom oscillators with phonon field. Sound wave in cubic box, of side length L, stationary waves are

$$\Phi = A \sin(n_x \pi x/L) \sin(n_y \pi y/L) \sin(n_z \pi z/L),$$

with frequency $\nu = cn/2L$, where c is here the speed of **sound** and $n \equiv \sqrt{n_x^2 + n_y^2 + n_z^2}$. The approximate number of modes in range $d\nu$ is

$$g(\nu)d\nu = \frac{1}{8}4\pi n^2 dn = \frac{4\pi V}{c^3}\nu^2 d\nu,$$

or more precisely

$$g(\nu)d\nu = 4\pi V(c_l^{-3} + 2c_t^{-3})\nu^2 d\nu,$$

where c_l and c_t are the longitudinal and transverse sound speeds. The maximum frequency is determined by

$$3N = \int_0^{\nu_m} g(\nu)d\nu = \frac{4\pi V}{3}(c_l^{-3} + 2c_t^{-3})\nu_m^3.$$

So

$$g(\nu)d\nu = 9N\nu_m^{-3}\nu^2 d\nu,$$

(v.s. Einstein's model, where only one frequency enters). Since phonons are bosons, use ω_{BE}, which is maximized by occupation numbers

$$N(\nu)d\nu = \frac{g(\nu)d\nu}{e^{h\nu/kT} - 1} = \begin{cases} 9N\nu_m^{-3}\frac{\nu^2 d\nu}{e^{h\nu/kT}-1} & \nu \leq \nu_m \\ 0 & \nu > \nu_m. \end{cases}$$

The total energy is

$$U = \int h\nu N(\nu)d\nu = \frac{9}{8}Nh\nu_m + 9Nh\nu_m^{-3}\int_0^{\nu_m}\frac{\nu^3 d\nu}{e^{h\nu/kT} - 1}.$$

This gives

$$C_V = 9Nkx_m^{-3}\int_0^{x_m}\frac{x^4 e^x}{(e^x - 1)^2}dx,$$

with $x_m \equiv h\nu_m/kT \equiv \theta_D/T$, where θ_D is the "Debye temperature." For $x_m \ll 1$ (high temperature), this gives $C_V \approx 3Nk$, as expected. For low temperature, this gives $C_V \approx \frac{1}{5}12\pi^4 Nk(T/\theta_D)^3$; valid for T below $0.1\theta_D \sim 10 - 20K$. Better fit to low-T data than Einstein's model.