11/30 Lecture outline

• Last time we started the following: first try at 1d SHO partition function:

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

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 N 3d H.O.s, $U = 3NkT$ and $C_V = 3Nk$, twice that of monatomic ideal gas.

We can do better: use the 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.

• 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.

• Debye's improvement: 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

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

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

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

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.