

III.7 Phonon gas: the Debye model of solids

Class schedule: April 23

Reading assignments: S22A-B, R10.2

Review: from the example of blackbody radiation, it is seen that the total energy of a particle system can be derived if we know (1) the occupation number $n(\epsilon)$, which is the mean number of particles in a given state as a function of the state energy ϵ and (2) the density of states, which is described as $dN_Q = g(\epsilon)d\epsilon$, or the number of quantum states in the energy range of ϵ and $\epsilon + d\epsilon$.

We calculate the number of quantum in the **phase space** by $N_Q = \frac{VV_p}{h^3}$, where V is the volume in the real space and V_p is the volume in the phase space and $dV_p = 4\pi p^2 dp$. Consider that the volume of the particles is constant, so $dN_Q = \frac{V}{h^3} dV_p = \frac{4\pi V}{h^3} p^2 dp$. For non-relativistic particles, $p = \sqrt{2m\epsilon}$, so

$$dN_Q = g(\epsilon)d\epsilon = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon$$

For relativistic particles, $p = \epsilon/c$, so

$$dN_Q = g(\epsilon)d\epsilon = \frac{4\pi V}{h^3 c^3} \epsilon^2 d\epsilon$$

Then the energy of the particle system is therefore given by $E = \int dE = \int n(\epsilon)\epsilon g(\epsilon)d\epsilon$. The integral is over all allowed energies. For photons, $\epsilon = h\nu$, so the integral is over all allowed frequencies of EM radiation, which spans from 0 to infinity. The result of photon statistics is the Planck's function.

In a very similar way, we may reach a more accurate calculation of internal energy and specific heat of solids. The Einstein model of solids does not accurately describe the specific heat at low temperatures measured in the laboratory. The Debye model treated vibrational modes of solids as matter waves (phonons) with a frequency distribution other than a single characteristic frequency as in the simplified Einstein model. Like photons, phonons are Bosons with zero chemical potential, and the energy of a phonon is $\epsilon = h\nu$. Unlike photons, there is an upper limit in the allowed phonon frequency ν_m determined by the mean distance between two particles.

Like photons, the density of states of phonons is given by $g(\epsilon)d\epsilon = 3 \times \frac{4\pi V}{h^3 c_s^3} \epsilon^2 d\epsilon$. The factor of 3 in the distribution is due to the fact that phonon waves have three polarization modes, one longitudinal and two transverse modes. Since $\epsilon = h\nu$, it follows, $g(\nu)d\nu = \frac{12\pi V}{c_s^3} \nu^2 d\nu$. And the total energy of solids is given by

$$E = \int_0^{\nu_m} h\nu n(\nu)g(\nu)d\nu = \frac{12\pi V h}{c_s^3} \int_0^{\nu_m} \frac{\nu^3}{e^{h\nu/kT} - 1} d\nu$$

With the constraint $\int_0^{\nu_m} g(\nu)d\nu = 3N_a$ for 1 mole of solid, we get

$$\frac{12\pi V}{c_s^3} \frac{1}{3} \nu_m^3 = 3N_a$$

Using this relation to replace terms in the expression of energy, we get

$$E = 9N_a kT \left(\frac{kT}{h\nu_m} \right)^3 \int_0^{h\nu_m/kT} \frac{x^3 dx}{e^x - 1}$$

Where $x = h\nu/(kT)$.

We define $\Theta_D = h\nu_m/k$ as Debye temperature, and $\epsilon_D = h\nu_m$ as Debye energy, then there is

$$E = 9N_a kT \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1}$$

The molar specific heat is $c_V = \partial E / \partial T$. It is seen that at high temperature $T \gg \Theta_D$, $E \approx 3N_a kT$ and $c_V \approx 3N_a k$. At low temperature $T \ll \Theta_D$, $E \propto T^4$, and $c_V \propto T^3$. The Debye model more accurately matches the laboratory measurements of c_V at low temperatures.