Heat capacities of solids

Any theory used to calculate lattice vibration heat capacities of crystalline solids must explain two things:

1. Near room temperature, the heat capacity of most solids is around 3k per atom (the molar heat capacity for a solid consisting of n-atom molecules is ~3nR). This is the well-known Dulong and Petit law.

2. At low temperatures, C_v decreases, becoming zero at T=0. Heat capacities have a temperature dependence of the form $\alpha T^3 + \gamma T$, where the T^3 term arises from lattice vibrations, and the linear term from conduction electrons.

Classical mechanics would predict $C_v = 3R$ at all temperatures, in violation of both experiment and the third law of thermodynamics.

<u>Einstein's theory of heat capacities</u>

Einstein treated the atoms in a crystal as N simple harmonic oscillators, all having the same frequency ν_E. The frequency ν_E depends on the strength of the restoring force acting on the atom, i.e. the strength of the chemical bonds within the solid. Since the equation of motion for each atom decomposes into three independent equations for the x, y and z components of displacement, and N-atom solid is equivalent to 3N harmonic oscillators, each vibrating independently at frequency ν_E. Note that this treatment is a gross approximation, since in reality the lattice vibrations are very complicated coupled oscillations.

The energy levels of the harmonic oscillators are given by

$$\varepsilon_v = h\nu_E(v + \tfrac{1}{2}), \qquad v = 0, 1, 2\ldots$$

Assuming the oscillators are in thermal equilibrium at temperature T, the partition function for a single oscillator is

$$q = \sum_{v=0}^{\infty} \exp[-\beta\varepsilon_v] = \sum_{v=0}^{\infty} \exp[-\beta h\nu_E(v+\tfrac{1}{2})] = e^{-x/2}\sum_{v=0}^{\infty} e^{-xv} = \frac{e^{-x/2}}{1-e^{-x}} \quad \text{where} \quad x = \beta h\nu_E.$$

In the above, we have used the fact that $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$.

The mean energy per oscillator is then

$$u = -\frac{d\ln q}{d\beta} = \frac{d}{d\beta}\left(\frac{\beta h\nu_E}{2} + \ln(1-e^{-\beta h\nu_E})\right) = \frac{h\nu_E}{2} + \frac{h\nu}{e^{\beta h\nu_E}-1}$$

The first term above, $h\nu/2$, is simply the zero point energy. Using the fact that energy is an extensive property, the energy of the 3N oscillators in the N-atom solid is

$$U = 3Nu = 3N\left(\frac{h\nu_E}{2} + \frac{h\nu}{e^{\beta h\nu_E}-1}\right)$$

The heat capacity at constant volume is therefore

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 3N\left(\frac{\partial U}{\partial \beta}\right)_v \frac{\partial \beta}{\partial T} = 3Nk\frac{x^2e^x}{(e^x-1)^2} \quad \text{where} \quad x = \frac{h\nu_E}{kT} = \frac{\theta_E}{T}$$

θ_E is the 'Einstein temperature', which is different for each solid, and reflects the rigidity of the lattice.

At the high temperature limit, when $T \gg \theta_E$ (and $x \ll 1$), the Einstein heat capacity reduces to $C_v = 3Nk$, the Dulong and Petit law [prove by setting $e^x \sim 1+x$ in the denominator].

At the low temperature limit, when $T \ll \theta_E$ (and $x \gg 1$), $C_v \rightarrow 0$ as $T \rightarrow 0$, as required by the third law of thermodynamics. [Prove by setting $e^x-1 \sim e^x$ in the denominator for large x].

Debye's theory of heat capacities

Debye improved on Einstein's theory by treating the coupled vibrations of the solid in terms of 3N normal modes of vibration of the whole system, each with its own frequency. The lattice vibrations are therefore equivalent to 3N independent harmonic oscillators with these normal mode frequencies. For low frequency vibrations, defined as those for which the wavelength is much greater than the atomic spacing, $\lambda \gg a$, the crystal may be treated as a homogeneous elastic medium. The normal modes are the frequencies of the standing waves that are possible in the medium.

Debye derived an expression for the number of modes with frequency between ν and $\nu+d\nu$ in such a medium.

$$g(\nu)\, d\nu = \frac{4\pi V\nu^2}{v^3}\, d\nu = \alpha\, \nu^2 d\nu$$

where V is the crystal volume and v is the propagation velocity of the wave. As outlined above, this expression applies only to low frequency vibrations in a crystal. Debye used the approximation that it applied to all frequencies, and introduced a maximum frequency ν_D (the Debye frequency) such that there were 3N modes in total. i.e. $\int_0^{\nu_D} g(\nu)d\nu = 3N$. The Debye frequency corresponds to $\lambda = 2a$, when neighbouring atoms vibrate in antiphase with each other. With this approximation in place, Debye integrated over all of the frequencies to find the internal energy of the crystal, and then calculated the heat capacity using $C_v = \left(\frac{\partial U}{\partial T}\right)_v$. The resulting expression is given below.

$$C_v = 3Nk\left(\frac{3}{{x_D}^3}\int_0^{x_D}\frac{x^4\, e^x\, dx}{(e^x - 1)^2}\right)$$

where $x = \frac{h\nu}{kT}$, and $x_D = \frac{h\nu_D}{kT} = \frac{\theta_D}{T}$. The Debye heat capacity depends only on the Debye temperature θ_D. The integral cannot be evaluated analytically, but the bracketed function is tabulated.

At high temperatures ($T \gg \theta_D$, $x_D \ll 1$), we may rewrite the integrand as follows:

$$\frac{x^4 e^x}{(e^x - 1)^2} = \frac{x^4}{(e^x - 1)(1 - e^x)} = \frac{x^4}{2(\cosh(x) - 1)} = \frac{x^4}{2(x^2/2! + x^4/4! + \dots)}$$

Retaining only the x^2 term in the denominator gives

$$C_v = 3Nk\left(\frac{3}{x_D{}^3}\int_0^{xD} x^2\, dx\right) = 3Nk$$

To determine the low temperature limit ($T \ll \theta_D, x_D \gg 1$), we note that the integrand tends towards zero rapidly for large x. This allows us to replace the upper limit by ∞ and turn the integral into a standard integral, to give

$$C_v = 3Nk\left(\frac{T}{\theta_D}\right)^3\left(3\int_0^{\infty}\frac{x^4 e^x}{(e^x - 1)^2}\right) = \frac{12}{5}\pi^4 Nk\left(\frac{T}{\theta_D}\right)^3$$

We see that the Debye heat capacity decreases as T^3 at low temperatures, in agreement with experimental observation. This is a marked improvement on Einstein's theory.