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.

Einstein's theory of heat capacities

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

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

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 $\displaystyle\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$.

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

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

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 $Cv = 3Nk$, 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 $x \gg 1$), $C_v \to 0$ as $T \to 0$, 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:

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

Retaining only the x^2 term in the denominator gives

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

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.

Free electron model of metals

Up to this point, we have only considered contributions to the heat capacity from vibrations within the solid. In metals, the free conduction electrons also contribute to the heat capacity. In the free electron model of metals, the conduction electrons are treated as a perfect gas obeying Fermi-Dirac statistics. Interactions of the electrons with the positively charged atomic ions and with the other electrons are neglected. This is not such a bad approximation as it may appear at first: the ions provide a positively charged background that partly screens the electrons from each other; and the residual collisions are often relatively unimportant - the energetically accessible final states are often already occupied, making any collisional excitation process forbidden by the Pauli exclusion principle.

The first step in deriving the heat capacity is to determine the density of states. We will first do this in momentum space, and then transform the result into an expression describing the density of states per unit energy.

The 3-dimensional Schrodinger equation for the translational motion of the electrons has the solutions

$$\phi_{n_1 n_2 n_3}(r) = A\, \sin\left(\frac{n_1 \pi x}{L}\right)\sin\left(\frac{n_2 \pi y}{L}\right)\sin\left(\frac{n_3 \pi z}{L}\right)$$

with $k = \left(\frac{\pi n_1}{L}, \frac{\pi n_2}{L}, \frac{\pi n_3}{L}\right)$ and $k^2 = \frac{\pi^2}{L^2}(n_1{}^2 + n_2{}^2 + n_3{}^2)$.

The allowed values of k therefore form a cubic point lattice in k-space, with spacing π/L and volume per point $(\pi/L)^3$. Finding the number of normal modes of the standing wave wavefunctions with k between k and $k+dk$ is equivalent to finding the number of lattice points between two spherical shells of radii k and $k+dk$ in the positive octant of k-space. The number of k-vectors of magnitude $\leq k$ is

$$n_k = \frac{\text{Volume of region}}{\text{Volume per point}} = \frac{(1/8)(4/3)\pi k^3}{(\pi/L)^3} = \frac{Vk^3}{6\pi^2} \quad \text{where } V = L^3.$$

The number $f(k)$ within an interval dk is found by differentiating this expression, giving

$$f(k)\,dk \;=\; \frac{dn_k}{dk}dk \;=\; \frac{Vk^2\,dk}{2\pi^2}$$

Since $k = 2\pi p/h$ (and therefore $dk = (2\pi/h)dp$), the density of states in momentum space is

$$f(p)\,dp = \frac{8\pi V p^2\,dp}{h^3}$$

where an extra factor of two has been added to account for the two possible spin states of the electrons. This expression may be converted to an energy density of states by substituting $\varepsilon = p^2/2m$ (and so $d\varepsilon = (p/m)dp$), to give

$$f(\varepsilon)\,d\varepsilon = \frac{4\pi V}{h^3}(2m)^{3/2}\,\varepsilon^{1/2}\,d\varepsilon$$

To determine the number of electrons with energies between ε and $\varepsilon+d\varepsilon$, we need to multiply the above expression, which gives the density of states at energy ε, with the probability $n(\varepsilon)$ of finding an electron in a given state with energy ε. Electrons are Fermions, and obey Fermi-Dirac statistics, so $n(\varepsilon)$ is given by the Fermi-Dirac distribution (Note: the Fermi-Dirac distribution is an analogue of the Boltzmann distribution for systems in which spin must be taken into account)

$$n(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon-\mu)] + 1} \qquad \text{where } \mu \text{ is the chemical potential and } \beta=1/kT$$

The number of electrons with energy between ε and $\varepsilon+d\varepsilon$ is then

$$dN(\varepsilon) \;=\; n(\varepsilon)f(\varepsilon)d\varepsilon \;=\; \frac{1}{\exp[\beta(\varepsilon-\mu)]+1}\frac{4\pi V}{h^3}(2m)^{3/2}\,\varepsilon^{1/2}\,d\varepsilon$$
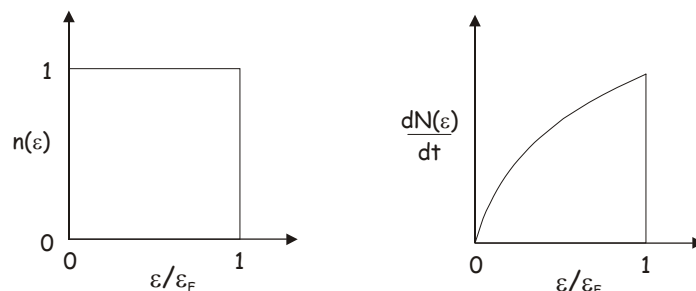
Integrating from zero to infinity gives the total number of electrons in the gas. The Fermi energy ε_F is the value of μ when T=0 i.e. $\varepsilon_F = \mu(0)$, and may also be written $\varepsilon_F = kT_F$, where T_F is the Fermi temperature.

Now we will look at the energy level occupations $n(e)$ and the overall energy distribution $N(\varepsilon)$ as the temperature is increased from zero.
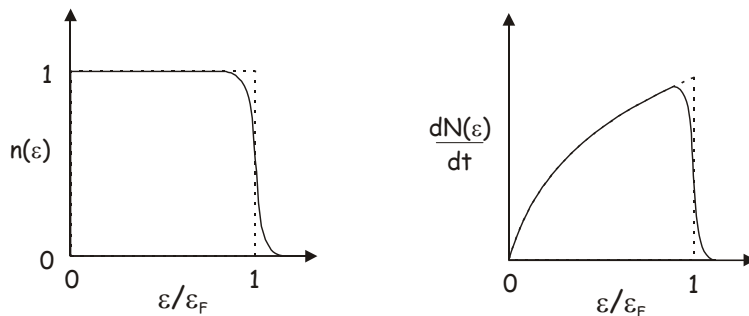
At T=0, the Fermi-Dirac distribution becomes

$$n(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon-\varepsilon_F)] + 1}$$

and since $\beta=\infty$ at T=0, this is equal to 0 if $\varepsilon > \varepsilon_F$ and 1 if $\varepsilon < \varepsilon_F$. The two distributions $n(\varepsilon)$ and $N(\varepsilon)$ are shown below.

At higher temperatures, the two distributions change slightly from their behaviour at T=0, due to electrons lying below the Fermi level being excited to states lying above the Fermi level. This is shown below.

Now we will consider the consequences of these distributions for the heat capacity. Classical mechanics would predict a contribution $\frac{1}{2}$ kT per electron to the heat capacity, in addition to the heat capacity arising from the lattice vibrations. This is a much larger contribution than is observed experimentally. The answer lies in the Fermionic nature of the electrons. In the classical model, a change in temperature ΔT would lead to an energy increase of around $k\Delta T$ per electron. However, we have seen that apart from electrons with energies very close to the Fermi energy ε_F, the states to which the electrons would be promoted by an energy increase of this magnitude are already occupied. Hence, only a very small fraction of electrons, those lying within $\sim k\Delta T$ of the Fermi level, are able to absorb the energy and contribute to the heat capacity.

The heat capacity per electron turns out to be

$$C_V = \frac{\pi^2}{2} k \frac{T}{T_F}$$

At room temperature this is a very small contribution to the overall heat capacity (on the order of a few percent). However, at very low temperatures the electronic heat capacity dominates, since it is linear in temperature while the lattice heat capacity is proportional to T^3.