Thermodynamics: Classical to Statistical

Prof. Sandip Paul

Department of Chemistry

Indian Institute of Technology Guwahati

Lecture – 31

Specific Heats of Solids

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Consider a simple solid consisting of ‘N’ number of atoms. The atoms in solid cannot translate (unlike liquids and gases). But, the atoms are free to vibrate about their equilibrium positions. Such vibrations are called lattice vibrations, and can be thought of as sound waves propagating through the crystal lattice. Each atom in a solid is specified by three independent position coordinates and three conjugate momentum coordinates.

Let us consider only small amplitude vibrations. In this case, we can expand the potential energy of interactions between the atoms to give an expression, which is quadratic in atomic displacements from their equilibrium positions. It is always possible to perform a normal mode analysis of the oscillations. In effect, we can find 3N independent modes of oscillations of the solids. Each mode of oscillation has its own particular frequency, and its own particular pattern of atomic displacements. Any general oscillation can be written as a linear combination of these normal modes.

Thus, it is clear that in normal mode coordinates the linearized lattice vibrations are equivalent to 3N independent harmonic oscillators (of course each oscillator corresponds to a different normal mode).

If the lattice vibrations behave classically, then according to equipartition theorem, each normal mode of oscillation has an associated mean energy k_BT in equilibrium at temperature T K, (1/2 k_BT due to kinetic energy of the oscillation and 1/2 k_BT for potential energy). The equipartition theorem says that every quadratic term in the energy expression gives 1/2 k_BT.

We have 3N normal modes of vibrations. Thus, the mean internal energy per mole (considering N equals to N_A) of solids is,

$$<E> = 3N_A k_BT = 3RT$$

The molar heat capacity or heat capacity per mole at constant volume is

$$C_V = \left(\frac{\partial <E>}{\partial T}\right)_V = 3R = 24.9 \text{ J mole}^{-1}\text{degree}^{-1}$$

In fact, at room temperature, most solids (in particular metals) have heat capacities which lie remarkably close to this value. This fact was discovered experimentally by Dulong and Petite at the beginning of the nineteenth century. But, Dulong and Petite's law, which is molar heat capacity of a solid is 24.9 J mole^{-1}degree^{-1}, is valid at high temperature only.

The molar heat capacity cannot remain a constant as the temperature approaches absolute zero. Since the equation,

$$S(T,V) = \int_0^T \frac{C_V(T)}{T} dT$$

suggests as $T \to 0$, entropy, $S \to \infty$, if C_V is constant, which violates third law of thermodynamics.

We can make a crude model of the behaviour of C_V at low temperatures by assuming that all the normal modes oscillate at the same frequency, ω, where,

$$\omega = 2\pi\nu$$

This approximation was first employed by Einstein. Thus the solid acts like a set of 3N independent oscillators and they vibrate at the same frequency. This is Einstein's model.

We know the average energy of 3N harmonic oscillators is,

$$< E > = 3N\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right)$$

The heat capacity is then,

$$C_V = \left(\frac{\partial < E >}{\partial T}\right)_V$$

Hence,

$$C_V = -\frac{3N\hbar\omega}{k_B T^2}\left[-\frac{e^{\beta\hbar\omega}\hbar\omega}{\left(e^{\beta\hbar\omega} - 1\right)^2}\right]$$

Simplifying, we get,

$$C_V = 3Nk_B\left(\frac{\hbar\omega}{k_B T}\right)^2\left[\frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}\right]$$

If we substitute, the value of Einstein temperature θ_E,

$$\theta_E = \frac{\hbar\omega}{k_B}$$

in the above expression of C_V, we get,

$$C_V = 3nR\left(\frac{\theta_E}{T}\right)^2 \left[\frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}} - 1\right)^2}\right]$$

When, $N = N_A$, $n = 1$, then molar heat capacity of solids is,

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2 \left[\frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}} - 1\right)^2}\right]$$

This is the general expression for molar heat capacity according to Einstein's Model.

- Now, we consider high temperature limit,

  $T >> \theta_E$ or $k_BT >> \hbar\omega$,

  Molar heat capacity becomes, $\overline{C_V} \approx 3R$,

  (considering $e^{\theta_E/T} = e^x = 1 + x + \frac{x^2}{2!} + ...$, so when x is very small, $e^{\theta_E/T} \approx 1$ and $\left(e^{\theta_E/T} - 1\right)^2 \approx \left(1 + \theta_E/T - 1\right)^2 \approx \left(\theta_E/T\right)^2$

- Considering the low temperature limit,

  $T << \theta_E$ or $\theta_E/T >> 1$

  $$C_V \approx 3R\left(\frac{\theta_E}{T}\right)^2 e^{-\frac{\theta_E}{T}}$$

  When, $\theta_E/T >> 1$, $\left(e^{\theta_E/T} - 1\right)^2 \approx e^{2\theta_E/T}$

  The specific heat approaches zero exponentially when T goes to 0.
  In reality, the specific heat of solids do not approach zero quite as quickly as suggested by Einstein's model when T tends to 0. The experimentally observed low temperature behaviour of C_V is $C_V \propto T^3$.

The reason for discrepancy is the crude approximation that all normal modes have the same frequency. In fact, long wavelength modes have lower frequencies than short wavelength modes, so, the former are harder to freeze out than the latter because the spacing between quantum energy levels, $\hbar\omega$ is smaller in the former case. The molar heat capacity does not decrease with temperature as rapidly as suggested by Einstein's Model, because those long wavelength modes are able to make significant contribution to heat capacity even at low temperatures.

A more realistic model of lattice vibrations was developed by the Dutch Physicist Peter Debye in 1912. In the Debye model, the frequencies of the normal modes of vibration are estimated by treating the solid as an isotropic continuous medium. This approach is reasonable because the modes which really matter at low temperatures are the long wavelength modes i.e., those whose wavelengths greatly exceeds the interatomic spacing.

It is plausible that these modes are not particularly sensitive to the discrete nature of the solid i.e., the fact that it is made up of atoms rather than being continuous.

Debye Theory of Solids

According to Debye theory,

$$C_V = 9Nk_B\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{\left(e^x-1\right)^2}dx \quad \textbf{(1)}$$

$$x = h\nu_D / k_B T \quad \text{and} \quad \theta_D = h\nu_D / k_B$$

Where θ_D is known as Debye Temperature and ν_D is the Debye frequency.

Let us consider a function D (Debye function), which is defined by

$$D = D\left(\frac{T}{\theta_D}\right) = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{\left(e^x-1\right)^2}dx \quad \textbf{(2)}$$

If we substitute the value of D from equation 2 into equation 1 we get,

$$C_V = 3Nk_B D\left(\frac{T}{\theta_D}\right) \quad \textbf{(3)}$$

Equation 3 must be evaluated numerically for arbitrary values of T/θ_D.

Now we consider two different temperature level.

- At high temperature,
  $\theta_D / T \to 0$, hence, x goes to 0. So, we can write,

$$\int_0^{\theta_D/T} \frac{x^4 e^x}{\left(e^x-1\right)^2}dx \approx \int_0^{\theta_D/T} \frac{x^4 \times 1}{\left(1+x-1\right)^2}dx = \int_0^{\theta_D/T} x^2 dx = \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3$$

So, if we substitute this in Debye expression of equation 2 we get $D(T/\theta_D) = 1$. Thus

$$C_V = 3Nk_B = 3nR$$

$$\overline{C_V} = 3R = 24.9 \text{ J mole}^{-1}\text{degree}^{-1}$$

So, Debye theory can predict the value of molar heat capacity of solids at high temperature.

- At the low temperature, $\theta_D / T \rightarrow \infty$, So

$$D\left(\frac{T}{\theta_D}\right) = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^\infty \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx$$

$$D = \frac{4\pi^4}{15} \times 3\left(\frac{T}{\theta_D}\right)^3 = \frac{4\pi^4}{5}\left(\frac{T}{\theta_D}\right)^3$$

$$C_V = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta_D}\right)^3$$

So $C_V \propto T^3$ and this is known as Famous T^3 law.

According to Debye theory heat capacity of solid, at high temperature, is a constant term 24.9 J mole^{-1}degree^{-1} as predicted by Dulong Petite’s law as well as Einstein’s model and at lower temperature limit C_V goes to T^3 according to Debye theory of solid.