

11.2: Heat Capacity of Solids

In the early 1800's French scientists Pierre Dulong and Alexis Petit noticed that many solid elements had near-identical per molar heat capacities as shown in Figure 11.6. This led to the Dulong–Petit law: $C_m = 3R$. Previously in Ch. 2 we encountered gases with such high heat capacities due to their three translational and three rotational motions, which imparts six degrees of freedom that rendered $C_m = 3R$ due to the equipartition theorem (Table 2.1). While this is perfectly understandable for a gas, it's hard to reconcile why heavy metallic elements such as lead and a gas such as methane have the same heat capacities. The answer is simple—solids have three (vibrational) potential energy and three kinetic energy degrees of freedom due to their bonding. Thus, the equipartition theorem still appears valid for solids, unless, those solids are cold, in which case something goes terribly wrong as shown in Figure 11.7.

From the data in Figure 11.7 we can see that, at low temperatures, solids of copper and tungsten have almost no heat capacity! And while it rises with temperature to the Dulong–Petit limit, it was quite the curiosity for many years why this behavior was observed in many materials. In fact, it was one of Albert Einstein's early contributions in 1907 to approximately describe the increase in heat capacity as vibrations in the solid state, called phonons, that behave just like Planck's photons. In this regard, instead of energy being related to the wavelength of light it was due to the frequency of an atomic vibration in the solid state. All one has to do is simply change the definition of average internal energy (U), as derived from the Boltzmann formula, from the Planck to the Einstein form: $\frac{1}{\lambda} \rightarrow \frac{1}{\lambda} \cdot \frac{h \cdot c}{\lambda}$

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$-1\}$ to $3N_A \cdot \frac{1}{\lambda} \cdot \frac{h \cdot c}{\lambda} \cdot \left\{ e^{\frac{1}{\lambda} \cdot \frac{h \cdot c}{\lambda} \cdot \frac{1}{k_B T}} - 1 \right\}^{-1}$. The prefactor is due to solids existing in 3 dimensions and that a mole has N_A number of atoms, and note that Einstein assumed that all the vibrations inside the solid had the same frequency ω . Since heat capacity is just the derivative of the internal energy with temperature, the result is:

$$\left[C = 3N_A \cdot \frac{\partial}{\partial T} \left(\frac{1}{\lambda} \cdot \frac{h \cdot c}{\lambda} \cdot \left\{ e^{\frac{1}{\lambda} \cdot \frac{h \cdot c}{\lambda} \cdot \frac{1}{k_B T}} - 1 \right\}^{-1} \right) \right] = 3N_A \cdot \frac{\partial}{\partial T} \left(\frac{1}{\lambda} \cdot \frac{h \cdot c}{\lambda} \right)$$

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$$\frac{\partial}{\partial T} = 3N_A \cdot \frac{\partial}{\partial T} \left(\frac{1}{\lambda} \cdot \frac{h \cdot c}{\lambda} \right)$$

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$$= 3N_A k_B \left(\frac{1}{\lambda} \cdot \frac{h \cdot c}{\lambda} \right)^2 \frac{1}{\left(e^{\frac{1}{\lambda} \cdot \frac{h \cdot c}{\lambda} \cdot \frac{1}{k_B T}} - 1 \right)^2} \cdot \left(e^{\frac{1}{\lambda} \cdot \frac{h \cdot c}{\lambda} \cdot \frac{1}{k_B T}} \right) \cdot \left(-\frac{1}{k_B T^2} \right)$$

This result correctly predicts that, as $T \rightarrow 0$ K, the heat capacity also $\rightarrow 0$ J/K/mol. At higher temperatures where: $e^{\frac{1}{\lambda} \cdot \frac{h \cdot c}{\lambda} \cdot \frac{1}{k_B T}} \sim 1 + \frac{1}{k_B T}$ we find that:

$$C \sim 3N_A k_B \left(\frac{1}{\lambda} \cdot \frac{h \cdot c}{\lambda} \right)^2 \frac{1 + \frac{1}{k_B T}}{\left(\frac{1}{k_B T} \right)^2} \sim 3N_A k_B \left(\frac{1}{\lambda} \cdot \frac{h \cdot c}{\lambda} \right)^2 \left(\frac{k_B T}{1} \right)^2 = 3N_A k_B = 3R$$

All of these results make us believe that Einstein has the correct approach; however, this turns out not to be the case! The problem is that the heat capacity rises exponentially in the Einstein model whereas in reality most materials have a $C_{p,m} \sim T^3$ behavior. And as shown by Peter Debye in 1912 this was due to Einstein's use of a single frequency for the solid-state vibrations, whereas there are a range of frequencies as shown in the inset of Figure 11.7.

The solution to address concerning the shortcoming of the Einstein model is to use a range of phonon frequencies to define the internal energy as so:

$$U = \int \text{degeneracy}(\omega) \cdot \langle \text{energy}(\omega) \rangle = \int \text{degeneracy}(\omega) \cdot \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} d\omega$$

So as not to labor the point one can show that the degeneracy of phonons as a function of frequency is $\frac{V\omega^2}{2\pi^2 v_s^3}$, where v_s is the speed of sound in the solid. As a result the Debye equation for the heat capacity of a solid is:

$$C = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T} \frac{V\omega^2}{2\pi^2 v_s^3} \int_0^{\omega_D} \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} d\omega \propto T^3$$

While we don't need to worry further about the mathematics of the result, suffice to say the result is proportional to T^3 as experimentally observed. It is also interesting to note that the upper limit of the Debye equation isn't infinity as one might expect. This is because Debye realized that there was an upper limit to the range of phonon frequencies as shown in Figure 11.8, which we will call the Debye frequency ω_D . Clearly, there cannot be a frequency higher than allowed by the atomic spacing. In practice, this upper limit is an empirical parameter that can be used to create a fit to experimental data.

Conclusion. The purpose of this chapter was to demonstrate that the Boltzmann formula has uses far beyond that encountered with the Maxwell-Boltzmann description of the velocities of gases. In terms of the development of physical chemistry as a science, it wasn't long after the phenomena of Blackbody radiation and the Debye theory of heat capacity were described that scientists started to make the connection between matter and waves. This ultimately resulted in quantum theory, which is the subject of the next chapter.

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