

## 22.6: Energy and Heat Capacity of the "Einstein Crystal"

In Section 22.4, we find an approximate partition function for the harmonic oscillator at high temperatures. Because it is a geometric series, the partition function for the harmonic oscillator can also be obtained exactly at any temperature. By definition, the partition function for the harmonic oscillator is

$$z = \sum_{n=0}^{\infty} \exp\left(\frac{-h\nu}{kT}\left(n + \frac{1}{2}\right)\right) = \exp\left(\frac{-h\nu}{2kT}\right) \sum_{n=0}^{\infty} \exp\left(\frac{-nh\nu}{kT}\right) = \exp\left(\frac{-h\nu}{2kT}\right) \sum_{n=0}^{\infty} \left[\exp\left(\frac{-h\nu}{kT}\right)\right]^n$$

This is just the infinite sum

$$z = a \sum_{n=0}^{\infty} r^n = \frac{a}{1-r}$$

with

$$a = \exp\left(\frac{-h\nu}{2kT}\right)$$

and

$$r = \exp\left(\frac{-h\nu}{kT}\right)$$

Hence, the exact partition function for the one-dimensional harmonic oscillator is

$$z = \frac{\exp(-h\nu/2kT)}{1 - \exp(-h\nu/kT)}$$

The partition function for vibration in each of the other two dimensions is the same. To get the partition function for oscillation in all three dimensions, we must sum over all possible combinations of the three energies. Distinguishing the energies associated with motion in the  $x$ -,  $y$ -, and  $z$ -directions by the subscripts  $n$ ,  $m$ , and  $p$ , respectively, we have for the three-dimensional harmonic oscillator:

$$\begin{aligned} z_{3D} &= \sum_{p=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \exp\left[\frac{-(\epsilon_n + \epsilon_m + \epsilon_p)}{kT}\right] \\ &= \sum_{p=0}^{\infty} \exp\frac{-\epsilon_p}{kT} \sum_{m=0}^{\infty} \exp\frac{-\epsilon_m}{kT} \sum_{n=0}^{\infty} \exp\frac{-\epsilon_n}{kT} \\ &= z^3 \end{aligned}$$

Hence,

$$z_{3D} = \left[ \frac{\exp(-h\nu/2kT)}{1 - \exp(-h\nu/kT)} \right]^3$$

and the energy of a crystal of  $N$ , independent, distinguishable atoms is

$$\begin{aligned} E &= N \langle \epsilon \rangle \\ &= NkT^2 \left( \frac{\partial \ln z_{3D}}{\partial T} \right)_V \\ &= \frac{3Nh\nu}{2} + \frac{3Nh\nu \exp(-h\nu/kT)}{1 - \exp(-h\nu/kT)} \end{aligned}$$

Taking the partial derivative with respect to temperature gives the heat capacity of this crystal. The molar heat capacity can be expressed in two ways that are useful for our purposes:

$$\begin{aligned}
 C_V &= \left( \frac{\partial \bar{E}}{\partial T} \right)_V \\
 &= 3\bar{N}k \left( \frac{h\nu}{kT} \right)^2 \left[ \frac{\exp(-h\nu/kT)}{(1 - \exp(-h\nu/kT))^2} \right] \\
 &= 3\bar{N}k \left( \frac{h\nu}{kT} \right)^2 \left[ \frac{\exp(h\nu/kT)}{(\exp(h\nu/kT) - 1)^2} \right]
 \end{aligned}$$

Consider the heat capacity at high temperatures. As the temperature becomes large,  $h\nu/kT$  approaches zero. Then

$$\exp\left(\frac{h\nu}{kT}\right) \approx 1 + \frac{h\nu}{kT}$$

Using this approximation in the second representation of  $C_V$  gives for the high temperature limit

$$\begin{aligned}
 C_V &\approx 3\bar{N}k \left( \frac{h\nu}{kT} \right)^2 \left[ \frac{1 + h\nu/kT}{(1 + h\nu/kT - 1)^2} \right] \\
 &\approx 3\bar{N}k \left( 1 + \frac{h\nu}{kT} \right) \\
 &\approx 3\bar{N}k = 3R
 \end{aligned}$$

Since  $C_V$  and  $C_P$  are about the same for solids at ordinary temperatures, this result is essentially equivalent to the law stated by Dulong and Petit. Indeed, it suggests that the law would be more accurate if stated as a condition on  $C_V$  rather than  $C_P$ , and this proves to be the case.

At low temperatures,  $h\nu/kT$  becomes arbitrarily large and  $\exp(-h\nu/kT)$  approaches zero. From the first representation of  $C_V$ , we see that

$$\lim_{T \rightarrow 0} \left( \frac{\partial \bar{E}}{\partial T} \right)_V = C_V = 0$$

In [Section 10.9](#), we see that  $C_P - C_V \rightarrow 0$  as  $T \rightarrow 0$ . Hence, the theory also predicts that  $C_P \rightarrow 0$  as  $T \rightarrow 0$ , in agreement with experimental results.

The Einstein model assumes that energy variations in a solid near absolute zero are entirely due to variations in the vibrational energy. From the assumption that all of these vibrational motions are characterized by a single frequency, it predicts the limiting values for the heat capacity of a solid at high and low temperatures. At intermediate temperatures, the quantitative predictions of the Einstein model leave room for improvement. An important refinement developed by Peter Debye assumes a spectrum of vibrational frequencies and results in excellent quantitative agreement with experimental values at all temperatures.

We can give a simple qualitative interpretation for the result that heat capacities decrease to zero as the temperature goes to absolute zero. The basic idea is that, at a sufficiently low temperature, essentially all of the molecules in the system are in the lowest available energy level. Once essentially all of the molecules are in the lowest energy level, the energy of the system can no longer decrease in response to a further temperature decrease. Therefore, in this temperature range, the heat capacity is essentially zero. Alternatively, we can say that as the temperature approaches zero, the fraction of the molecules that are in the lowest energy level approaches one, and the energy of the system of  $N$  molecules approaches the smallest value it can have.

The weakness in this qualitative view is that there is always a non-zero probability of finding molecules in a higher energy level, and this probability changes as the temperature changes. To firm up the simple picture, we need a way to show that the energy decreases more rapidly than the temperature near absolute zero. More precisely, we need a way to show that

$$\lim_{T \rightarrow 0} \left( \frac{\partial \bar{E}}{\partial T} \right)_V = C_V = 0$$

Since the Einstein model produces this result, it constitutes a quantitative validation of our qualitative model.

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