

The curve in Figure 16.11 of the text shows how the vibrational heat capacity depends on temperature. Note that even when the temperature is only slightly above the vibrational temperature, the heat capacity is close to its equipartition value.

The total heat capacity of a molecular substance is the sum of each contribution (Figure 16.12 of the text). When equipartition is valid (when the temperature is well above the characteristic temperature of the mode $T \gg \theta_M$) we can estimate the heat capacity by counting the numbers of modes that are active. In gases, all three translational modes are always active and contribute $\frac{3}{2}R$ to the molar heat capacity. If we denote the number of active rotational modes by ν_R^\ddagger (so for most molecules at normal temperatures $\nu_R^\ddagger = 2$ for linear molecules, and 3 for non-linear molecules), then

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \dots$$

The equipartition value $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R$ is reached when the temperature is high enough so that $T \gg \theta_M$ for all the modes. However, if the temperature is lower, then the modes with higher characteristic temperatures are not active, and the heat capacity is lower than the equipartition value. The number of active modes is ν_R^\ddagger for all temperatures in the range $\theta_{M,1} < T < \theta_{M,2}$, and all modes are active in the range $T > \theta_{M,2}$. The average heat capacity is $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R$ for all temperatures in the range $\theta_{M,1} < T < \theta_{M,2}$. In the intermediate range $\theta_{M,1} < T < \theta_{M,2}$ the heat capacity is a smooth curve, starting from $\frac{3}{2}R$ at the lower temperature and approaching the equipartition value at the higher temperature.

Solutions to exercises

16.1 The thermal energy is given by $\epsilon = \frac{1}{2}m\omega^2 x^2$ and the energy of the harmonic oscillator is $\epsilon = \frac{1}{2}m\omega^2 x^2$. The energy of the harmonic oscillator is $\epsilon = \frac{1}{2}m\omega^2 x^2$.

$$\epsilon = \frac{1}{2}m\omega^2 x^2 = \frac{1}{2}m\omega^2 \left(\frac{h}{2\pi m\nu} \right)^2$$

where ν is the vibrational frequency, and h is Planck's constant.

$$\epsilon = \frac{1}{2}m\omega^2 \left(\frac{h}{2\pi m\nu} \right)^2 = \frac{1}{2}m\omega^2 \frac{h^2}{4\pi^2 m^2 \nu^2} = \frac{h^2 \omega^2}{4\pi^2 m \nu^2} = \frac{h^2 \omega^2}{4\pi^2 m \nu^2}$$

16.2 The energy is

$$\epsilon = \frac{1}{2}m\omega^2 x^2 = \frac{1}{2}m\omega^2 \left(\frac{h}{2\pi m\nu} \right)^2 = \frac{h^2 \omega^2}{4\pi^2 m \nu^2}$$

16.3 $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \dots$

where ν_R^\ddagger is the number of active rotational modes.

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