A Derivation of the Equipartition Theorem

The general derivation of the equipartition theorem involves statistical mechanics beyond the scope of our discussions, so we will do a special case using a familiar classical system, simple harmonic oscillators each consisting of a particle moving in one dimension under the action of an elastic restoring force such as a spring with force constant κ. The kinetic energy of the particle at any instant is $mv_x^2/2$ and its potential energy is $\kappa x^2/2$, so the total energy is

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}\kappa x^2 \qquad \textbf{8-15}$$

From Equation 8-1, the Boltzmann distribution is

$$f_B(E) = Ae^{-E/kT} = Ae^{-(mv_x^2/2kT + \kappa x^2/2kT)} \qquad \textbf{8-16}$$

The probability that an oscillator will have energy E corresponding to v_x in dv_x and x in dx will be

$$f_B(E)dx\, dv_x = Ae^{-(mv_x^2/2kT + \kappa x^2/2kT)}dx\, dv_x \qquad \textbf{8-17}$$

where the constant A is determined from the normalization condition that the total probability is 1; that is,

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} Ae^{-(mv_x^2/2kT + \kappa x^2/2kT)}\, dx\, dv_x = 1 \qquad \textbf{8-18}$$

This rearranges to

$$A\int_{-\infty}^{+\infty} e^{-(mv_x^2/2kT)}dv_x \int_{-\infty}^{+\infty} e^{-(\kappa x^2/2kT)}\, dx = 1 \qquad \textbf{8-19}$$

Each of the two integrals in Equation 8-19 are of the same form. With the aid of Table B1-1, we have

$$A = \left(\frac{m}{2\pi kT}\right)^{1/2}\left(\frac{\kappa}{2\pi kT}\right)^{1/2} \qquad \textbf{8-20}$$

The average energy of an oscillator is then given by

$$\langle E \rangle = \int\int E f_B(E)dx\, dv_x = A\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\left(\frac{1}{2}mv_x^2 + \frac{1}{2}\kappa x^2\right)e^{-(mv_x^2/2kT)}e^{e^{-(\kappa x^2/2kT)}}dx\, dv_x$$

$$\textbf{8-21}$$

$$\langle E \rangle = A \int_{-\infty}^{+\infty} \frac{1}{2} m v_x^2 e^{-(mv_x^2/2kT)} dv_x \int_{-\infty}^{+\infty} e^{-(\kappa x^2/2kT)} dx$$

$$+ A \int_{-\infty}^{+\infty} e^{-(mv_x^2/2kT)} dv_x \int_{-\infty}^{+\infty} \frac{1}{2} \kappa x^2 e^{-(\kappa x^2/2kT)} dx \qquad \textbf{8-22}$$

Notice that the first term in Equation 8-22 is the integral of the kinetic energy times $f_B(E)$, that is, it is the average kinetic energy of the oscillator. Similarly, the second term is the average potential energy. These integrals may also be evaluated with the aid of Table B1-1. The result, when multiplied by A as given by Equation 8-20, yields

$$\langle E \rangle = \left(\frac{1}{2} m v_x^2 \right)_{avg} + \left(\frac{1}{2} \kappa x^2 \right)_{avg} = \frac{1}{2} kT + \frac{1}{2} kT = kT \qquad \textbf{8-23}$$

The important features of this result are (1) that both the average kinetic energy and the average potential energy depend *only* on the absolute temperature and (2) that each average value is equal to $\frac{1}{2}kT$. This result for the harmonic oscillator is a special case of the general equipartition of energy theorem:

In equilibrium, each degree of freedom contributes $\frac{1}{2}kT$ to the average energy per molecule.