More

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 $\frac{1}{2}mv_x^2$ and its potential energy is $\frac{1}{2}\kappa x^2$, so the total energy is

$$E = \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}\kappa x^2 \tag{8-38}$$

From Equation 8-13 the Boltzmann distribution is

$$f_B(E) = Ae^{-E/kT} = Ae^{-(mv_x^2/2kT + \kappa x^2/2kT)} \tag{8-39}$$

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

$$f_B(E)\, dx\, dv_x = Ae^{-(mv_x^2/2kT + \kappa x^2/2kT)}\, dx\, dv_x \tag{8-40}$$

where the constant A is determined from the normalization condition that the total probability is 1, i.e.,

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} Ae^{-(mv_x^2/2kT + \kappa x^2/2kT)}\, dx\, dv_x = 1 \tag{8-41}$$

This rearranges to

$$A\int_{-\infty}^{+\infty} e^{-mv_x^2/2kT}\, dx_x \int_{-\infty}^{+\infty} e^{-\kappa x^2/2kT}\, dx = 1 \tag{8-42}$$

The two integrals in Equation 8-42 are both of the same form. With the aid of Table B1-1, we have

$$A = \left(\frac{m}{2\pi kT}\right)^{1/2}\left(\frac{\kappa}{2\pi kT}\right)^{1/2} \tag{8-43}$$

The average energy of an oscillator is then given by

$$\begin{aligned}\langle E\rangle &= \int\int E\, f_B(E)\, dx\, dv_x \\ &= A\int_{-\infty}^{+\infty} (\tfrac{1}{2}\, mv_x^2 + \tfrac{1}{2}\, \kappa x^2)e^{-mv_x^2/2kT}\, e^{-\kappa x^2/2kT}\, dx\, dv_x\end{aligned} \tag{8-44}$$

Continued

$$\langle E \rangle = A \int_{-\infty}^{+\infty} \tfrac{1}{2} m v_x^2 e^{-m v_x^2/2kT} \, dv_x \int_{-\infty}^{+\infty} e^{-\kappa x^2/2kT} \, dx + A \int_{-\infty}^{+\infty} e^{-m v_x^2/2kT} \, dv_x \int_{-\infty}^{+\infty} \tfrac{1}{2} \kappa x^2 e^{-\kappa x^2/2kT} \, dx \qquad \textbf{8-45}$$

Notice that the first term in Equation 8-45 is the integral of the kinetic energy times $f_B(E)$, i.e., 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 8-43, yields

$$\langle E \rangle = (\tfrac{1}{2} m v_x^2)_{\text{av}} + (\tfrac{1}{2} \kappa x^2)_{\text{av}} = \tfrac{1}{2} kT + \tfrac{1}{2} kT = kT \qquad \textbf{8-46}$$

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.**