Harmonic oscillators

Our proof of the equipartition theorem depends crucially on the classical approximation. To see how quantum effects modify this result, let us examine a particularly simple system which we know how to analyze using both classical and quantum physics: *i.e.*, a simple harmonic oscillator. Consider a one-dimensional harmonic oscillator in equilibrium with a heat reservoir at temperature T. The energy of the oscillator is given by

$$E = \frac{p^2}{2\,m} + \frac{1}{2}\kappa\,x^2, \tag{467}$$

where the first term on the right-hand side is the kinetic energy, involving the momentum p and mass m, and the second term is the potential energy, involving the displacement x and the force constant κ. Each of these terms is quadratic in the respective variable. So, in the classical approximation the equipartition theorem yields:

$$\frac{\overline{p^2}}{2\,m} = \frac{1}{2}\,k\,T, \tag{468}$$

$$\frac{1}{2}\kappa\,\overline{x^2} = \frac{1}{2}\,k\,T. \tag{469}$$

That is, the mean kinetic energy of the oscillator is equal to the mean potential energy which equals $(1/2)\,k\,T$. It follows that the mean total energy is

$$\overline{E} = \frac{1}{2}\,k\,T + \frac{1}{2}\,k\,T = k\,T. \tag{470}$$

According to quantum mechanics, the energy levels of a harmonic oscillator are equally spaced and satisfy

$$E_n = (n+1/2)\,\hbar\,\omega, \tag{471}$$

where n is a non-negative integer, and

$$\omega = \sqrt{\frac{\kappa}{m}}. \tag{472}$$

The partition function for such an oscillator is given by

$$Z = \sum_{n=0}^{\infty} \exp(-\beta\,E_n) = \exp[-(1/2)\,\beta\,\hbar\,\omega] \sum_{n=0}^{\infty} \exp(-n\,\beta\,\hbar\,\omega). \tag{473}$$

Now,

$$\sum_{n=0}^{\infty} \exp(-n\,\beta\,\hbar\,\omega) = 1 + \exp(-\beta\,\hbar\,\omega) + \exp(-2\,\beta\,\hbar\,\omega) + \cdots \tag{474}$$

is simply the sum of an infinite geometric series, and can be evaluated immediately,

$$\sum_{n=0}^{\infty} \exp(-n\,\beta\,\hbar\,\omega) = \frac{1}{1-\exp(-\beta\,\hbar\,\omega)}. \tag{475}$$

Thus, the partition function takes the form

$$Z = \frac{\exp[-(1/2)\,\beta\,\hbar\,\omega]}{1-\exp(-\beta\,\hbar\,\omega)}, \tag{476}$$

and

$$\ln Z = -\frac{1}{2}\,\beta\,\hbar\,\omega - \ln[1-\exp(-\beta\,\hbar\,\omega)] \tag{477}$$

The mean energy of the oscillator is given by [see Eq. (399)]

$$\overline{E} = -\frac{\partial}{\partial\beta}\ln Z = -\left[-\frac{1}{2}\,\hbar\,\omega - \frac{\exp(-\beta\,\hbar\,\omega)\,\hbar\,\omega}{1-\exp(-\beta\,\hbar\,\omega)}\right], \tag{478}$$

or

$$\overline{E} = \hbar\,\omega\left[\frac{1}{2} + \frac{1}{\exp(\beta\,\hbar\,\omega)-1}\right]. \tag{479}$$

Consider the limit

$$\beta\,\hbar\,\omega = \frac{\hbar\,\omega}{k\,T} \ll 1, \tag{480}$$

in which the thermal energy $k\,T$ is large compared to the separation $\hbar\,\omega$ between the energy levels. In this limit,

$$\exp(\beta\,\hbar\,\omega) \simeq 1 + \beta\,\hbar\,\omega, \tag{481}$$

so

$$\overline{E} \simeq \hbar\,\omega \left[\frac{1}{2} + \frac{1}{\beta\,\hbar\,\omega}\right] \simeq \hbar\,\omega \left[\frac{1}{\beta\,\hbar\,\omega}\right], \tag{482}$$

giving

$$\overline{E} \simeq \frac{1}{\beta} = k\,T. \tag{483}$$

Thus, the classical result (470) holds whenever the thermal energy greatly exceeds the typical spacing between quantum energy levels.

Consider the limit

$$\beta\,\hbar\,\omega = \frac{\hbar\,\omega}{k\,T} \gg 1, \tag{484}$$

in which the thermal energy is small compared to the separation between the energy levels. In this limit,

$$\exp(\beta\,\hbar\,\omega) \gg 1, \tag{485}$$

and so

$$\overline{E} \simeq \hbar\,\omega\,[1/2 + \exp(-\beta\,\hbar\,\omega)] \simeq \frac{1}{2}\,\hbar\,\omega. \tag{486}$$

Thus, if the thermal energy is much less than the spacing between quantum states then the mean energy approaches that of the ground-state (the so-called *zero point* energy). Clearly, the equipartition theorem is only valid in the former limit, where $k\,T \gg \hbar\,\omega$, and the oscillator possess sufficient thermal energy to explore many of its possible quantum states.

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