

18.1: Energy Distributions and Energy Levels

Beginning in [Chapter 20](#), we turn our attention to the distribution of energy among the molecules in a closed system that is immersed in a constant-temperature bath, that is at equilibrium, and that contains a large number of molecules. We want to find the probability that the energy of a molecule in such a system is in a particular interval of energy values. This probability is also the fraction of the molecules whose energies are in the specified interval, since we assume that these statements mean the same thing for a system at equilibrium.

The probability that the energy of a particular molecule is in a particular interval is intimately related to the energies that it is possible for a molecule to have. Before we can make further progress in describing molecular energy distributions, we must discuss atomic and molecular energies. For our development of the Boltzmann equation, we need to introduce the idea of quantized energy states. This requires a short digression on the basic ideas of quantum mechanics and the quantized energy levels of atoms and molecules.

We have derived two expressions that relate the energy of a molecule to the probability that the molecule will have that energy. One follows from the barometric formula

$$\begin{aligned}\eta(h) &= \eta(0) \exp\left(\frac{-mgh}{kT}\right) \\ &= \eta(0) \exp\left(\frac{-\epsilon_{\text{potential}}}{kT}\right)\end{aligned}$$

in which the number density of molecules depends exponentially on their gravitational potential energy, mgh , and the reciprocal of the temperature. From the barometric formula, we can find the probability density function

$$\frac{df}{dh} = \frac{mg}{kT} \exp\left(\frac{-mgh}{kT}\right)$$

(See problem 3.22) The other is the Maxwell-Boltzmann distribution function

$$\frac{df}{dv} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(\frac{-mv^2}{2kT}\right) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(\frac{-\epsilon_{\text{kinetic}}}{2kT}\right)$$

in which the probability density of molecular velocities depends exponentially on their kinetic energies, $mv^2/2$, and the reciprocal of the temperature. We will see that this dependence is very general. Any time the molecules in a system can have a range of energies, the probability that a molecule has energy ϵ is proportional to $\exp(-\epsilon/kT)$. The exponential term, $\exp(-\epsilon/kT)$, is often called the Boltzmann factor.

We might try to develop a more general version of the Maxwell-Boltzmann distribution function by an argument that somehow parallels our derivation of the Maxwell-Boltzmann equation. It turns out that any such attempt is doomed to failure, because it is based on a fundamentally incorrect view of nature. In developing the barometric formula and the Maxwell-Boltzmann distribution, we assume that the possible energies are continuous; a molecule can be at any height above the surface of the earth, and its translational velocity can have any value. When we turn to the distribution of other ways in which molecules can have energy, we find that this assumption produces erroneous predictions about the behavior of macroscopic collections of molecules.

The failure of such attempts led Max Planck to the first formulation of the idea that energy is quantized. The spectrum of light emitted from glowing-hot objects (so-called “black bodies”) depends on the temperature of the emitting object. Much of the experimentally observable behavior of light can be explained by the hypothesis that light behaves like a wave. Mechanical (matter-displacement) waves carry energy; the greater the amplitude of the wave, the more energy it carries. Now, light is a form of energy, and a spectrum is an energy distribution. It was a challenge to late nineteenth century physics to use the wave model for the behavior of light to predict experimentally observed emission spectra. This challenge went unmet until Planck introduced the postulate that such “black-body radiators” absorb or emit electromagnetic radiation only in discrete quantities, called quanta. Planck proposed that the energy of one such quantum is related to the frequency, ν , of the radiation by the equation $E = h\nu$, where the proportionality constant, h , is now called **Planck’s constant**. In Planck’s model, the energy of an electromagnetic wave depends on its frequency, not its amplitude.

In the years following Planck’s hypothesis, it became clear that many properties of atoms and molecules are incompatible with the idea that an atom or molecule can have any arbitrary energy. We obtain agreement between experimental observations and

theoretical models only if we assume that atoms and molecules can have only very particular energies. This is observed most conspicuously in the interactions of atoms and molecules with electromagnetic radiation. One such interaction gives rise to a series of experimental observations known as the photoelectric effect. In order to explain the photoelectric effect, Albert Einstein showed that it is necessary to extend Planck's concept to assume that light itself is a stream of discrete energy quanta, called photons. In our present understanding, it is necessary to describe some of the properties of light as wave-like and some as particle-like.

In many absorption and emission spectra, we find that a given atom or molecule can emit or absorb electromagnetic radiation only at very particular frequencies. For example, the light emitted by atoms excited by an electrical discharge contains a series of discrete emission lines. When it is exposed to a continuous spectrum of frequencies, an atom is observed to absorb light at precisely the discrete frequencies that are observed in emission. Niels Bohr explained these observations by postulating that the electrons in atoms can have only particular energies. The absorption of visible light by atoms and molecules occurs when an electron takes up electromagnetic energy and moves from one discrete energy level to a second, higher, one. (Absorption of a continuous range of frequencies begins to occur only when the light absorbed provides sufficient energy to separate an electron from the original chemical species, producing a free electron and a positively charged ion. At the onset frequency, neither of the product species has any kinetic energy. Above the onset frequency, spectra are no longer discrete, and the species produced have increasingly greater kinetic energies.) Similar discrete absorption lines are observed for the absorption of infrared light and microwave radiation by diatomic or polyatomic gas molecules. Infrared absorptions are associated with vibrational motions, and microwave absorptions are associated with rotational motions of the molecule about its center of mass. These phenomena are explained by the quantum theory.

The quantized energy levels of atoms and molecules can be found by solving the Schrödinger equation for the system at hand. To see the basic ideas that are involved, we discuss the Schrödinger equation and some of the most basic approximations that are made in applying it to the description of atomic and molecular systems. But first, we should consider one more preliminary question: If the quantum hypothesis is so important to obtaining valid equations for the distribution of energies, why are the derivations of the Maxwell-Boltzmann equation and the barometric formula successful? Maxwell's derivation is successful because the quantum mechanical description of a molecule's translational kinetic energy is very well approximated by the assumption that the molecule's kinetic energy can have any value. In the language of quantum mechanics, the number of translational energy levels available to a molecule is very large, and successive energy levels are very close together—so close together that it is a good approximation to say that they are continuous. Similarly, the gravitational potential energies available to a molecule in the earth's atmosphere are well approximated by the assumption that they belong to a continuous distribution.

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