

**COPYRIGHT NOTICE:**

Donald W. Rogers: Einstein's *Other* Theory

is published by Princeton University Press and copyrighted, © 2005, by Princeton University Press. All rights reserved. No part of this book may be reproduced in any form by any electronic or mechanical means (including photocopying, recording, or information storage and retrieval) without permission in writing from the publisher, except for reading and browsing via the World Wide Web. Users are not permitted to mount this file on any network servers.

For COURSE PACK and other PERMISSIONS, refer to entry on previous page. For more information, send e-mail to [permissions@pupress.princeton.edu](mailto:permissions@pupress.princeton.edu)

# One

---

## History

IN 1819 DULONG AND PETIT enunciated a principle, which now bears their names, that the atomic weight of a solid element times its specific heat is a constant. In modern units,

$$\text{at wt.} \times \text{sp. heat} \cong 6 \text{ cal K}^{-1} \text{ mol}^{-1} \cong 25 \text{ J K}^{-1} \text{ mol}^{-1}$$

where J is the joule and K is the kelvin. The modern term for (at wt.  $\times$  sp. heat) is the *molar heat capacity*, designated  $C_V$  when measured at constant volume. (In the nineteenth century there was some dispute over whether the heat capacity should be measured at constant pressure or constant volume, but it soon became clear that  $C_V$  is more appropriate for our purposes.)

### 1.1 Failure of the Dulong-Petit Law

Historically, the law of Dulong and Petit settled several disputes about the atomic weights of solids, but we are principally interested in cases in which it fails. Boltzmann argued that the specific heat of a system can be rationalized on the basis of  $\frac{1}{2}\kappa T$  of energy per degree of freedom of molecular motion where  $\kappa$  is a suitable constant (see below) and  $T$  is the temperature. Unfortunately, by the time this ingenious argument had been put forth, numerous violations of the law were known and the whole argument was discredited. Boltzmann's explanation was substantially correct but something radical had to be done to modify it.

Einstein noticed that the law of Dulong and Petit fails badly for diamond. Subsequent low-temperature studies showed that it always fails, provided the temperature is low enough. Whenever the law fails for simple crystals, the observed Dulong and Petit constant is smaller than it "ought to be." Later cryoscopic studies showed that the Dulong and Petit constant is always "too small" at some temperature and that it approaches zero near 0 K, a temperature region unattainable at the time of Einstein's original work. Einstein set out only to remedy problems in predicting the heat capacity of diamond but in so doing he developed a general theory of the variation of  $C_V$  with  $T$  for all solids at all temperatures, even down to 0 K.

## 1.2 Crystals: Einstein's View

Einstein contemplated a model of harmonic oscillators free to move in three dimensions tethered to regularly spaced lattice points by isotropic restraining forces. By isotropic, we mean that there are no differences in the forces in the  $x$ ,  $y$ , and  $z$  directions.

By the early twentieth century, it was known that the energy of a *classical* mechanical system is  $\frac{1}{2}\kappa T$  per degree of freedom per particle or  $\frac{1}{2}RT$  per degree of freedom per mole, where  $R$  is the ideal gas constant, which has a modern value of  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ . The three-dimensional harmonic oscillator has three degrees of freedom contributing to its kinetic energy and three degrees of freedom contributing to its potential energy, leading to  $\frac{6}{2}RT = 3RT$  of energy. From classical thermodynamics,

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad (1.2.1)$$

where  $U$  is the molar energy; hence

$$C_V = 3R = 3(8.31) = 24.9 \text{ J K}^{-1} \text{ mol}^{-1}.$$

So it is that the law of Dulong and Petit is consistent with classical mechanics. The question is: Why does it fail for diamond? This Einstein deduced in 1906 on the basis of the recent (1900) quantum theory of Max Planck. It soon became evident that his deduction is valid for very many solids at low temperatures.

If the harmonic oscillators in a simple crystal have discrete levels of energy as Planck proposed, then they should all be at the lowest level at  $T = 0 \text{ K}$ . Very near that temperature, at  $T \cong 0 \text{ K}$ , an infinitesimal temperature rise would not be sufficient to promote any of the atoms in the crystal to the next higher (first excited) quantum state. No promotion, no energy absorption. If there is no energy absorption for an infinitesimal temperature rise,

$$dU = C_V dT = 0 \quad (1.2.2)$$

and, since  $dT \neq 0$ ,  $C_V$  must be zero.

Now we have the two extremes of heat capacity for a simple crystal. At very low temperatures  $C_V \cong 0$  and at high temperatures  $C_V \cong 24.9 \text{ J K}^{-1} \text{ mol}^{-1}$ . The question is what happens in between.

### PROBLEMS

- 1.1. How much heat energy (in joules) does it take to heat a kilogram of copper from 20.0 to 40.0 K?

- 1.2. How much heat energy in joules does it take to heat a kilogram of water from 20.0 to 40.0 K? Recall (or look up) the historic definition of the calorie.
- 1.3. Do the answers to problems 1.1 and 1.2 give scientific support to the folk saying, “A watched pot never boils”?

# Two

---

## Background

THE SIMPLE MECHANICAL SYSTEM of the classical harmonic oscillator underlies important areas of modern physical theory. This chapter develops the basic model in one, two, and three dimensions. The concept of degeneracy arises in the two-dimensional oscillation of a square plate or diaphragm. Three-dimensional harmonic oscillation relates to oscillatory modes in the Rayleigh-Jeans equation (section 4.6). Vibration of a macroscopic three-dimensional crystal is treated by Debye's theory in chapter 6. Harmonic oscillator theory is important when it succeeds and also when it fails, as we shall see in the motivation to find a theory of radiation that we now call the quantum theory, described at the end of this chapter.

### 2.1 Classical Harmonic Motion

Motion of a mass  $m$  under the influence of a Hooke's law force  $f$  acting on  $m$  such that it moves back and forth along a straight line across an equilibrium point is *simple harmonic motion* (SHM):

$$f = -kx \quad (2.1.1)$$

(see figure 2.1.1) In a one-dimensional  $x$  space, the force is directly proportional and opposite to the displacement  $x$  of the mass away from the equilibrium position, which we define as  $x = 0$ . At  $x = 0$ ,  $f = 0$ . The proportionality constant  $k$  is called a Hooke's law force constant. The sign on the right is negative because the force is opposite to the displacement, that is, it is a *restoring force*.

According to Newton's second law,

$$f = ma, \quad (2.1.2)$$

where the acceleration  $a$  is  $d^2x/dt^2$  for motion along the single space coordinate  $x$ . Equating Hooke's law and Newton's law,

$$\begin{aligned} m \frac{d^2x}{dt^2} &= -kx, \\ \frac{d^2x}{dt^2} &= -\frac{k}{m}x, \end{aligned} \quad (2.1.3)$$

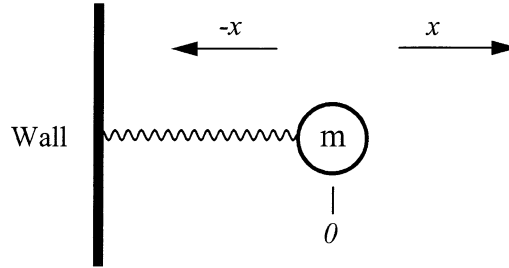


Figure 2.1.1. Harmonic oscillator of one mass.

which is the Newton-Hooke equation of motion for a harmonic oscillator of a single mass. Equation 2.1.3 has, as one of its solutions,

$$x = Ae^{i\omega t} \quad (2.1.4)$$

where  $\omega = \sqrt{k/m}$  and  $i = \sqrt{-1}$ . Sine and cosine solutions like  $x = A \sin \omega t$  also exist as can be seen by substituting any of the solutions

$$\begin{aligned} x &= A e^{i\omega t}, \\ x &= A \sin \omega t, \\ x &= A \cos \omega t \end{aligned} \quad (2.1.5)$$

into the Newton-Hooke equation for the harmonic oscillator. A general rule for equations of this kind is that the sum or difference of two or more solutions is also a solution. This can be verified by substituting an appropriate sum or difference into the Newton-Hooke equation.

In a *conservative system* in which there is no frictional or similar loss in energy, the force is related to the *potential energy*  $V$  by

$$V = - \int f dx; \quad (2.1.6)$$

hence, for the Hooke's law force,

$$V = - \int_0^x -kx dx = \frac{1}{2} kx^2. \quad (2.1.7)$$

The total energy  $E$  is *kinetic energy*  $T$  plus potential energy  $V$ ,

$$E = \frac{1}{2} m \left( \frac{dx}{dt} \right)^2 + \frac{1}{2} kx^2, \quad (2.1.8)$$

where  $dx/dt$  is a velocity if its direction is specified (a vector) or a speed if the direction is ignored (a scalar).

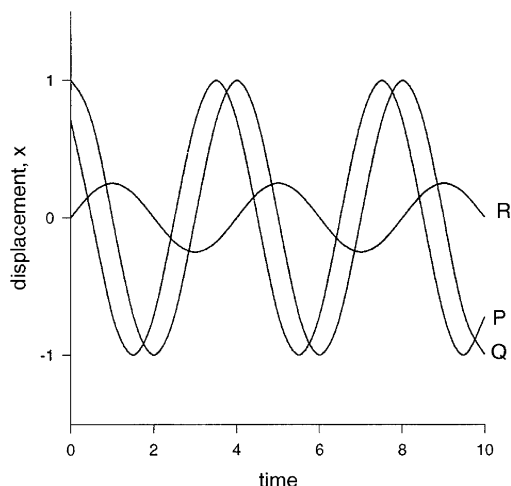


Figure 2.1.2. The function  $x = f(t)$  for a linear harmonic oscillator of one mass. Time  $t$  is measured in units of  $\pi/2\omega$ . One period  $\tau$  is 4 units on the  $t$  axis. The initial condition is  $x(0) = 0.707$  distance unit for trajectory P, 1.00 for trajectory Q, and 0.0 distance units for trajectory R. The second initial condition is  $\dot{x} = 0.707, 0.0,$  and 0.250 speed units for P, Q, and R respectively.

The locus of positions versus time over a specified period  $t - t_0$  is a *trajectory* (figure 2.1.2). Any simple harmonic trajectory can be represented by

$$x = A \cos(\omega t + \phi) \quad (2.1.9a)$$

or by

$$x = A \sin(\omega t + \theta), \quad (2.1.9b)$$

where  $A$  is the maximum amplitude (maximum excursion of the mass) and  $\phi$  and  $\theta$  are phase angles which locate the sine wave on the time axis. The sine and cosine descriptions of a harmonic oscillator trajectory differ only by a change of  $\pi/2$  in the phase angle; hence, as already said, they are equally valid solutions of the Newton-Hooke equation. Integrating a second-order differential equation twice produces two constants of integration. Once we have characterized a frictionless harmonic oscillator by specifying two constants, for example,  $A$  and  $\phi$ , there is nothing more we can say about it. We have used up both of the two constants of integration allowed by the second-order Newton-Hooke differential equation.

## 2.2 Wave Equations: The Vibrating String

Suppose a vibrating guitar string resembles figure 2.2.1a at some instant in time,  $t$ . Let the displacement from the equilibrium position  $u(x, t) = 0$  of some infinitesimal part of the string be  $u(x, t)$  on the vertical axis. Each infinitesimal length of the string is undergoing harmonic motion about  $u(x, t) = 0$  in response to a vertical force. There is no horizontal motion and no net force in the horizontal direction. The tension  $\tau$  at any point of the string is the magnitude of the force acting at that point. The tension is tangential to the string. Because there is no net horizontal force, the  $x$  components of the force at any two points of the string must be equal and opposite. The tension on two *adjacent* points, being a scalar, is the same for each.

Figure 2.2.1b shows a tangent line drawn at an arbitrary point on the string  $u(x, t)$  between the end points  $x = 0$  and  $x = L$ . Figures 2.2.2a and b show this part of the string in more detail. Let  $\alpha$  be the angle between the horizontal and the tangent at  $x$ . Let  $\beta$  be the angle between the horizontal

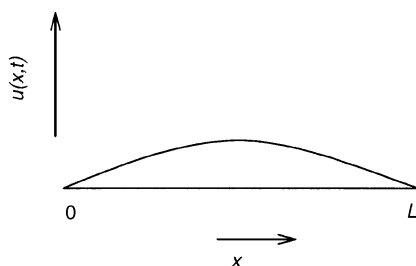


Figure 2.2.1a. The fundamental mode of vibration of a stretched string of length  $L$ . The horizontal line is the equilibrium position of the string.

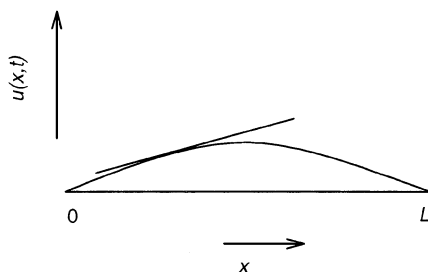


Figure 2.2.1b. The fundamental mode of vibration of a stretched string of length  $L$ . A line has been drawn tangent to  $u(x, t)$  at an arbitrary value of  $x$ .

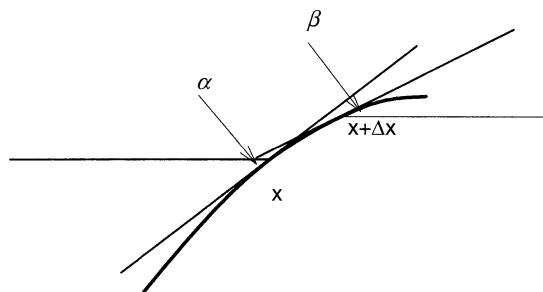


Figure 2.2.2a. Angles  $\alpha$ , between the horizontal and the tangent at  $x$ , and  $\beta$ , between the horizontal and  $x + \Delta x$ . On this part of the wave,  $\alpha > \beta$ .

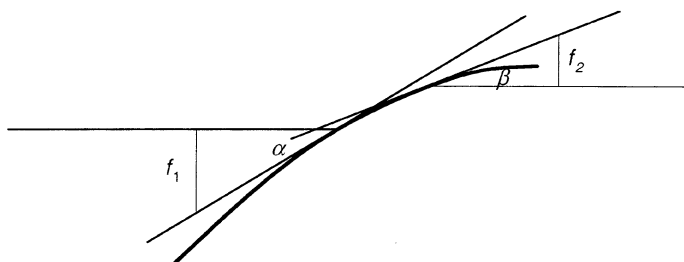


Figure 2.2.2b. Magnitudes of the vertical (transverse) forces  $f_1$  and  $f_2$  acting on the string at  $x$  and  $x + \Delta x$ .

and another tangent drawn at a slightly different point,  $x + \Delta x$ . The points are not quite adjacent because  $\Delta x$  is finite.

We would like to know how  $u(x, t)$  changes with  $x$  and  $t$ , that is, we would like to find a partial differential equation relating  $u$ ,  $x$ , and  $t$ . The magnitude of the vertical force  $f_2$  on the string at  $x + \Delta x$  differs from the magnitude of the vertical force  $f_1$  at  $x$  by

$$\tau_2 \sin \beta - \tau_1 \sin \alpha = f_2 - f_1. \quad (2.2.1)$$

The magnitude of the force on the string segment of length  $\Delta x$  and unit thickness is, by Newton's second law,  $f = ma$ , where  $m$  is the mass of the segment (density  $\rho$  times  $\Delta x$ ) and the transverse acceleration is  $a = \partial^2 u(x, t) / \partial t^2$ , so

$$\tau_2 \sin \beta - \tau_1 \sin \alpha = \rho \Delta x \frac{\partial^2 u(x, t)}{\partial t^2}. \quad (2.2.2)$$

Because the horizontal components of the force at  $x$  and  $x + \Delta x$  are equal and opposite, their magnitudes are equal:

$$\tau_2 \cos \beta = \tau_1 \cos \alpha = \tau$$

where  $\tau$  is the tension of the unpluck string. We can divide equation 2.2.2 by the horizontal component, which gives

$$\frac{\tau_2 \sin \beta}{\tau_2 \cos \beta} - \frac{\tau_1 \sin \alpha}{\tau_1 \cos \alpha} = \frac{\rho \Delta x}{\tau} \frac{\partial^2 u(x, t)}{\partial t^2} \quad (2.2.3)$$

or

$$\tan \beta - \tan \alpha = \frac{\rho \Delta x}{\tau} \frac{\partial^2 u(x, t)}{\partial t^2}. \quad (2.2.4)$$

The tangents are the slopes at  $x$  and  $x + \Delta x$ ,

$$\left( \frac{\partial u(x, t)}{\partial x} \right)_{x+\Delta x} - \left( \frac{\partial u(x, t)}{\partial x} \right)_x = \frac{\rho \Delta x}{\tau} \frac{\partial^2 u(x, t)}{\partial t^2} \quad (2.2.5)$$

or

$$\frac{\left( \frac{\partial u(x, t)}{\partial x} \right)_{x+\Delta x} - \left( \frac{\partial u(x, t)}{\partial x} \right)_x}{\Delta x} = \frac{\rho}{\tau} \frac{\partial^2 u(x, t)}{\partial t^2}, \quad (2.2.6)$$

but the difference in magnitude between two slopes with respect to a change in  $x$  approaches the curvature  $\partial^2 u(x, t) / \partial x^2$  as  $\Delta x$  approaches zero (that is, as the points become more nearly adjacent). This yields

$$\frac{\partial^2 u(x, t)}{\partial x^2} = \frac{\rho}{\tau} \frac{\partial^2 u(x, t)}{\partial t^2} \quad (2.2.7)$$

which is the wave equation we sought.

### 2.3 Wave Motion

A known tension can be placed on a uniform string, for example, by using it to suspend a weight from a fixed beam. When this is done and a sharp transverse pulse is given near one end of the string, the pulse travels along the string with a pulse velocity of magnitude  $v$ . Experimentally, one finds that

$$v = \sqrt{\frac{\tau}{\rho}} \quad (2.3.1)$$

where  $\tau$  is the magnitude of the initial tension on the wire and  $\rho$  is its uniform density. (Tension imparted by the pulse is transverse and does not affect the coaxial component of the tension.) If a train of waves is

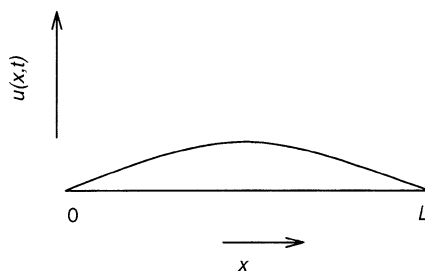


Figure 2.3.1. The fundamental mode of vibration of a stretched string of length  $L$ . The function  $u(x, t)$  describes one-half of a sine wave.

created by sequential pulses, the train travels at the same speed as a single pulse. For the purpose of studying electromagnetic radiation, we shall be especially interested in sinusoidal wave trains. With the substitution  $v^2 = \tau/\rho$  from equation 2.3.1, we can write the wave equation

$$\frac{\partial^2 u(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u(x, t)}{\partial t^2}. \quad (2.3.2)$$

If the speed and the wavelength of a sinusoidal wave train are both known, we also know the frequency

$$v = \frac{v}{\lambda} \quad (2.3.3)$$

where  $v$ , the magnitude of the velocity  $\mathbf{v}$ , is the speed (be careful to distinguish the speed  $v$  from the frequency  $\nu$ ) and  $\lambda$  is the wavelength. The frequency in equation 2.3.3 is expressed in hertz. One hertz is a complete cycle per second. Because of the analogy between circular motion and harmonic motion, frequencies are often expressed as  $\omega$ , measured in radians per second. The conversion is  $\omega = 2\pi\nu$ . In electromagnetic theory, confusion between  $\nu$  and  $v$  is avoided by calling the speed of electromagnetic radiation  $c$ . In a vacuum,  $c$  is a constant,  $c = 2.998 \times 10^8 \text{ m s}^{-1}$ . In dense media such as water or glass, the speed of light is considerably less than  $c$  (see chapter 9).

Figure 2.3.1 shows the lowest frequency (longest wavelength) that can be produced by striking a string with fixed ends that is  $L$  meters long. The wave shown is one-half of a sine wave, so the permissible standing waves on this string have  $\lambda = 2L, 2L/2, 2L/3, \dots$  corresponding to frequencies of  $\nu_0, \nu_1, \nu_2, \dots$ . A guitar string at 440 Hz (A natural) would have overtones at 880, 1320,  $\dots$  Hz. An infinite number of frequencies is possible for the vibrating string but, for real strings, overtones diminish rapidly and only a few contribute to the perceived tone of the instrument.

At higher frequencies, inertial mass and resistance to bending damp the oscillation. A real string is not a conservative system.

## 2.4 Solving the Wave Equation: Separation of Variables

Assume that the wave function  $u(x, t)$  can be separated into two parts, one a function of  $x$  and one a function of  $t$ :

$$u(x, t) = X(x)T(t). \quad (2.4.1)$$

We verify this assumption by showing that physically plausible results arise from the solutions of the wave equations that are obtained using it. Under the assumption of separability, the wave equation

$$\frac{\partial^2 u(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u(x, t)}{\partial t^2} \quad (2.4.2)$$

can be written

$$T(t) \frac{d^2 X(x)}{dx^2} = \frac{1}{v^2} X(x) \frac{d^2 T(t)}{dt^2}. \quad (2.4.3)$$

If we divide by  $u(x, t) = X(x)T(t)$ , we get

$$\frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} = \frac{1}{v^2 T(t)} \frac{d^2 T(t)}{dt^2}. \quad (2.4.4)$$

The variables  $x$  and  $t$  are independent. If we hold  $t$  constant, the left-hand side of the separated equation is equal to a constant no matter what the value of  $x$ . If the left-hand side of the equation is equal to a constant, the right-hand side is equal to the same constant, no matter what the value of  $t$ . Let us call the constant  $-\beta^2$ :

$$\frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} = -\beta^2 \quad (2.4.5)$$

and

$$\frac{1}{v^2 T(t)} \frac{d^2 T(t)}{dt^2} = -\beta^2. \quad (2.4.6)$$

That is,

$$\frac{d^2 X(x)}{dx^2} + \beta^2 X(x) = 0 \quad (2.4.7)$$

and

$$\frac{d^2 T(t)}{dt^2} + \beta^2 v^2 T(t) = 0, \quad (2.4.8)$$

where  $v$  is the speed of the wave and  $-\beta^2$  is called a *separation constant*. Let us call these two equations the  $X(x)$  equation and the  $T(t)$  equation. The constant  $-\beta^2$  is written as a square to maintain an analogy with  $\omega^2$  in the harmonic oscillator equation. The sign of  $-\beta^2$  is chosen to bring about an oscillatory solution such as we found for the physical system of a real harmonic oscillator. If  $\beta$  were positive, the solution would not be oscillatory.

## 2.5 The Time-Independent Wave Equation $X(x)$

The Newton-Hooke equation for the harmonic oscillator

$$\frac{d^2x}{dt^2} = -\frac{k}{m}x \quad (2.5.1)$$

can be written

$$\frac{1}{x(t)} \frac{d^2x(t)}{dt^2} = -\frac{k}{m} = -\omega^2 \quad (2.5.2)$$

or

$$\frac{d^2x(t)}{dt^2} + \omega^2x(t) = 0 \quad (2.5.3)$$

where  $\omega = \sqrt{k/m}$  is the frequency of harmonic oscillation. The sign of  $\omega^2$  is in agreement with the separation constant  $-\beta^2$  in the  $X(x)$  equation, so as to bring about an oscillatory solution.

In treating the harmonic oscillator, we were led to many solutions, among which are

$$x(t) = Ae^{i\omega t},$$

$$x(t) = A \sin \omega t,$$

$$x(t) = A \cos \omega t, \quad (2.5.4a)$$

$$x(t) = A \cos(\omega t + \phi),$$

and

$$x(t) = A \cos \omega t \pm B \sin \omega t, \quad (2.5.4b)$$

where the sum and difference of two solutions is a solution by the *superposition principle*. A mathematical statement of the superposition principle is that, if  $u_1$  and  $u_2$  are solutions of a linear homogeneous partial

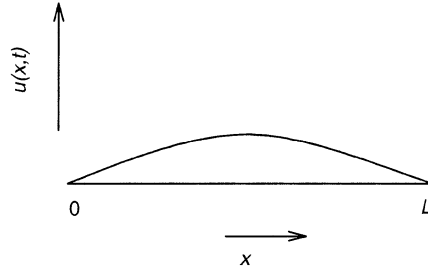


Figure 2.5.1. Vibration of a string fixed at each end (fundamental mode). The maximum of the displacement function (antinode) does not move.

*differential equation, then*

$$u = c_1 u_1 + c_2 u_2 \quad (2.5.5)$$

*is also a solution*, where  $c_1$  and  $c_2$  are arbitrary constants.

In the same way, the  $X(x)$  equation

$$\frac{d^2 X(x)}{dx^2} + \beta^2 X(x) = 0$$

leads to many solutions, including

$$\begin{aligned} X(x) &= A \cos \beta x \pm B \sin \beta x, \\ X(x) &= B \sin(\beta x + \phi), \end{aligned} \quad (2.5.6a)$$

or

$$X(x) = B \cos(\beta x + \theta), \quad (2.5.6b)$$

where the only difference between the sin and cos solutions is the phase angle (see figure 2.1.2). In the solution

$$X(x) = B \sin \beta x \quad (2.5.6c)$$

we have arbitrarily set the phase angle  $\phi = 0$ . This amounts to the boundary condition  $X(x) = 0$  at  $x = 0$  in figure 2.5.1. Two boundary conditions are allowed for a second-order differential equation. The second boundary condition that must be satisfied by a string fixed at both ends is  $X(x) = B \sin \beta x = 0$  at  $x = L$ . The amplitude constant  $B$  cannot be zero because, if it were,  $X(x)$  would be zero for the entire length of the string (a trivial solution involving no vibration at all). Therefore  $\sin \beta x = 0$  at  $x = L$ .

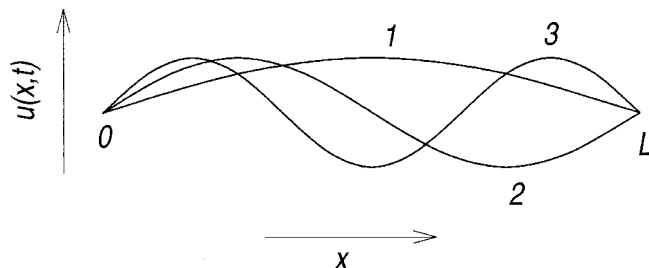


Figure 2.5.2. Standing vibratory waves (fundamental, first, and second overtones) in a string fixed at each end. The integers  $n = 1, 2, 3, \dots$  correspond to different modes of vibration.

The condition  $\sin \beta x = 0$  is also satisfied by  $\sin n\pi = 0$ , where  $n$  is a positive integer (see figure 2.1.2). Now, if

$$B \sin \beta L = B \sin n\pi, \quad n = 1, 2, 3, \dots, \quad (2.5.7)$$

then

$$\begin{aligned} \beta L &= n\pi, \\ \beta &= \frac{n\pi}{L}, \quad n = 1, 2, 3, \dots, \end{aligned} \quad (2.5.8)$$

and the second boundary condition leads to

$$X(x) = B \sin \frac{n\pi x}{L}, \quad n = 1, 2, 3, \dots, \quad (2.5.9)$$

for the time-independent part of the wave equation. The wave does not move; hence it is called a *standing wave*. The integers  $n = 1, 2, 3, \dots$  describe the fundamental *mode* and the first, second,  $\dots$  *overtone*s of the vibration. These modes are called the first, second, third,  $\dots$  *harmonics*. The mode of vibration with  $n = 2$  is the second harmonic but it is the first overtone. The mode with  $n = 3$  is the third harmonic but the second overtone, and so on.

The term *node* (not to be confused with mode) is used to designate the point at which the wave function crosses the  $u(x, t) = 0$  axis for a standing wave. For example, the fundamental mode of vibration in figure 2.5.2 has only two nodes, one at each end of the string. Higher harmonics have, sequentially, more nodes. The number of nodes for each harmonic is  $n + 1$ . One sometimes sees the term *internal nodes*, implying exclusion of the two terminal nodes, which must, obviously, be the same for all harmonics. The number of internal nodes is  $n - 1$ .

Remember that the number of waves per second times the wavelength (distance covered) of each wave is its speed in distance per second,

$v\lambda = v = \omega\lambda/2\pi$ . The more nodes a wave function has, the shorter the wavelength and the higher the frequency for a given speed of propagation  $v$ . The energy imparted to a string by initially striking or plucking it is quickly distributed among the fundamental and overtones, but the amount of energy retained by the overtones diminishes rapidly with increasing  $n$ , which is why the tone we hear is dominated by the fundamental. Thus the vertical axis in figure 2.5.2 is an energy axis. Each new harmonic increases the energy of the vibration on the vertical axis.

## 2.6 The Time-Dependent Wave Equation $T(t)$

For the time-dependent equation, we have

$$\frac{d^2T(t)}{dt^2} + \beta^2v^2T(t) = 0. \quad (2.6.1)$$

This wave equation is quite analogous to the Newton-Hooke equation, describing the variation of  $T(t)$  with time as the independent variable. The function  $T(t)$  oscillates harmonically with  $\beta^2v^2$  as the *fundamental frequency*  $\omega_1$ . (The notation  $\omega_0$  is often used for the fundamental frequency but we shall use  $\omega_1$  to preserve correspondence between  $\omega_n$  and  $n\pi x/L$ .) The possibility of higher harmonics (overtones) gives rise to a *spectrum of frequencies*  $\omega_n$ , of which the fundamental frequency is the lowest.

A general solution of the time-dependent wave equation is

$$T(t) = C \cos \omega_n t + D \sin \omega_n t, \quad \omega_n = \beta v = n\pi v/L. \quad (2.6.2)$$

There are no boundary conditions analogous to those for the standing wave, but we already know from the standing wave that  $\beta = n\pi/L$ ,  $X(x) = B \sin(n\pi x/L)$ , and from the separation of variables equation we have

$$u(x, t) = X(x)T(t); \quad (2.6.3)$$

hence

$$u(x, t) = B \sin \frac{n\pi x}{L} (C \cos \omega_n t + D \sin \omega_n t) \quad (2.6.4)$$

where  $X(x)$  is one of the solutions that we can select from those given as equations 2.5.4 with the slight modification of  $\omega_n$  for  $\omega$  to give the entire energy spectrum. Collecting constants, the complete equation is

$$u(x, t) = (E \cos \omega_n t + F \sin \omega_n t) \sin \frac{n\pi x}{L}. \quad (2.6.5)$$

By the superposition principle, the sum of solutions for different values of  $n$  is also a solution,

$$u(x, t) = \sum_{n=1}^{\infty} (E \cos \omega_n t + F \sin \omega_n t) \sin \frac{n\pi x}{L}. \quad (2.6.6)$$

An equivalent form is

$$u(x, t) = \sum_{n=1}^{\infty} G_n \cos(\omega_n t + \phi_n) \sin \frac{n\pi x}{L} = \sum_{n=1}^{\infty} u_n(x, t). \quad (2.6.7)$$

Each  $u(x, t)$  in  $\sum_{n=1}^{\infty} u_n(x, t)$  is a *normal mode* and the sum  $\sum_{n=1}^{\infty} u_n(x, t)$  is the *superposition* of normal modes.

## 2.7 Superpositions

The fundamental of a standing wave is

$$u(x, t) = G_1 \cos(\omega_1 t) \sin \frac{\pi x}{L} \quad (2.7.1)$$

where  $\phi = 0$  and  $n = 1$ . We have, from 2.6.2,  $\omega_1 = \pi v/L$ ; hence the frequency in hertz is

$$\frac{\omega_1}{2\pi} = \frac{v}{2L} \quad (2.7.2)$$

and  $\omega_1 t = \pi v t/L$ , which leads to

$$u(x, t) = G_1 \sin \frac{\pi x}{L} \cos(\omega_1 t) = G_1 \sin \frac{\pi x}{L} \cos \frac{\pi v t}{L}. \quad (2.7.3)$$

From the trigonometric identity,

$$\sin \xi \cos \zeta = \frac{1}{2} \sin(\xi + \zeta) + \frac{1}{2} \sin(\xi - \zeta), \quad (2.7.4)$$

we have

$$u(x, t) = \frac{G_1}{2} \sin \left( \frac{\pi x}{L} + \frac{\pi v t}{L} \right) + \frac{G_1}{2} \sin \left( \frac{\pi x}{L} - \frac{\pi v t}{L} \right) \quad (2.7.5)$$

$$= \frac{G_1}{2} \sin \left[ \frac{\pi}{L} (x + vt) \right] + \frac{G_1}{2} \sin \left[ \frac{\pi}{L} (x - vt) \right]. \quad (2.7.6)$$

For the fundamental mode, the wavelength of a standing wave is  $\lambda = 2L$ ; hence

$$u(x, t) = \frac{G_1}{2} \sin \left[ \frac{2\pi}{\lambda} (x + vt) \right] + \frac{G_1}{2} \sin \left[ \frac{2\pi}{\lambda} (x - vt) \right]. \quad (2.7.7)$$

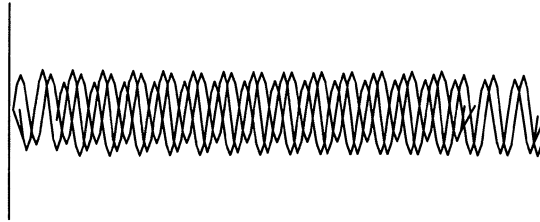


Figure 2.7.1. Destructive interference occurs when boundary conditions are not satisfied.

This is a superposition of two *running* waves  $\rightarrow$  and  $\leftarrow$ . (If a wave is not standing, we say it is running.) We can think of these terms as describing a running wave  $\rightarrow$  that strikes a barrier at  $L$  and is reflected back  $\leftarrow$  toward  $x = 0$ . If the boundary conditions  $u = 0$  at  $x = 0$  and  $L$  are satisfied, the wave is undamped and, if it were not for frictional losses, it would last forever. If the boundary conditions are not satisfied, *destructive interference takes place and the wave disappears in finite time.*

Figure 2.7.1 shows destructive interference as it occurs between waves that are bouncing back and forth between the right and left boundaries. The positive amplitudes cancel the negative amplitudes at each point on the wave, yielding a zero sum.

## 2.8 A Two-Dimensional Wave Equation

The two-dimensional wave equation satisfied by a vibrating thin sheet of dimensions  $x_1 \times x_2$  (see figure 2.8.1),

$$\frac{\partial^2 u(x_1, x_2, t)}{\partial x_1^2} + \frac{\partial^2 u(x_1, x_2, t)}{\partial x_2^2} = \frac{1}{v^2} \frac{\partial^2 u(x_1, x_2, t)}{\partial t^2}, \quad (2.8.1)$$

has  $u(x_1, x_2, t)$  as a function of space  $x_1, x_2$  and time  $t$ .

As in the one-dimensional wave equation, the two-dimensional surface equation can be separated into a space part and a time part. The separability assumption

$$u(x_1, x_2, t) = F(x_1, x_2)T(t) \quad (2.8.2)$$

leads to

$$\frac{1}{F(x_1, x_2)} \left[ \frac{\partial^2 F(x_1, x_2)}{\partial x_1^2} + \frac{\partial^2 F(x_1, x_2)}{\partial x_2^2} \right] = \frac{1}{v^2 T(t)} \frac{d^2 T(t)}{dt^2}. \quad (2.8.3)$$

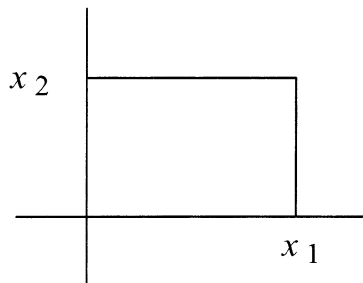


Figure 2.8.1. A thin sheet capable of vibrating in the directions perpendicular to  $x_1$  and  $x_2$ .

The parts are identically equal only if

$$\frac{\partial^2 F(x_1, x_2)}{\partial x_1^2} + \frac{\partial^2 F(x_1, x_2)}{\partial x_2^2} + \beta^2 F(x_1, x_2) = 0 \quad (2.8.4)$$

and

$$\frac{d^2 T(t)}{dt^2} + \beta^2 v^2 T(t) = 0, \quad (2.8.5)$$

where  $-\beta^2$  is the separation constant.

## 2.9 The Time-Independent Wave Functions $X(x_1)$ and $X(x_2)$

The space part can be separated a second time to obtain an  $x_1$  part and an  $x_2$  part. We assume that  $F(x_1, x_2) = X(x_1)X(x_2)$ , which leads to

$$\frac{1}{X(x_1)} \frac{d^2 X(x_1)}{dx_1^2} = -\rho^2 \quad (2.9.1)$$

and

$$\frac{1}{X(x_2)} \frac{d^2 X(x_2)}{dx_2^2} = -\sigma^2, \quad (2.9.2)$$

where the relation among separation constants is  $\rho^2 + \sigma^2 = \beta^2$ . These equations yield solutions

$$X(x_1) = A \cos \rho x_1 + B \sin \rho x_1 \quad (2.9.3)$$

and

$$X(x_2) = C \cos \sigma x_2 + D \sin \sigma x_2. \quad (2.9.4)$$

The boundary conditions at  $x_1 = x_2 = 0$  force  $A = 0$  and  $C = 0$ . At  $x_1 = L_1$  and  $x_2 = L_2$ ,

$$\rho L_1 = n_1 \pi \text{ and } \sigma L_2 = n_2 \pi, \quad n_1 = 1, 2, 3, \dots, \quad n_2 = 1, 2, 3, \dots,$$

whence

$$\beta = \pi \left( \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} \right)^{1/2}. \quad (2.9.5)$$

Now there are two integers  $n_1$  and  $n_2$  which determine the nodal properties of the standing vibration in two dimensions.

The time-dependent equation yields

$$T(t) = E \cos \omega t + F \sin \omega t$$

or, using the phase angle  $\phi$ ,

$$T(t) = G \cos(\omega t + \phi), \quad (2.9.6)$$

where

$$\omega = v\beta = v\pi \left( \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} \right)^{1/2}. \quad (2.9.7)$$

The complete solution is a double sum,

$$\begin{aligned} u(x_1, x_2, t) &= \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} H \cos(\omega t + \phi) \sin \frac{n_1 \pi x}{L_1} \sin \frac{n_2 \pi x}{L_2} \\ &= \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} u(x_1, x_2, t). \end{aligned} \quad (2.9.8)$$

The motion has fundamental modes of vibration, harmonics, nodes, and antinodes as in one-dimensional wave motion. Waves perpendicular to one another on a square surface lead to the possibility of *degeneracy*. If  $L_1 = L_2 = L$ , different modes of motion in the  $x_1$  and  $x_2$  directions can lead to the same frequency  $\omega$ :

$$\omega = \frac{v\pi}{L} (n_1^2 + n_2^2)^{1/2}. \quad (2.9.9)$$

For example, the combinations  $n_1 = 1, n_2 = 2$  and  $n_1 = 2, n_2 = 1$ , although they correspond to distinctly different vibrations on the surface pictured in figure 2.9.1, lead to the same  $\omega$  and hence to the same total energy of vibration.

The relation between  $\omega$  and the integers  $n_1$  and  $n_2$  shows that the higher the integers, the higher  $\omega$ , and hence the higher the energy of the vibration.

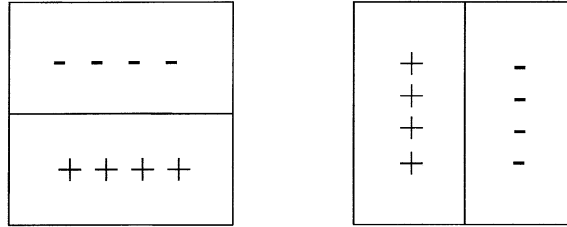


Figure 2.9.1. Degenerate modes of vibration on a square planar surface. The  $-$  surface goes down into the plane of the page and the  $+$  surface comes out of the plane of the page. The straight lines are nodal lines.

We shall want, ultimately, to know the energy density for vibrations within a selected geometry as a function of the frequency of the waves that satisfy the boundary conditions imposed by the geometry.

## 2.10 A Three-Dimensional Wave Equation

Extension to three dimensions yields an equation that is analogous to the two-dimensional case. Suppose vibrations occur in a cubic solid. (Other geometries work, but a cube gives simpler equations.) If destructive interference is not to occur, all three components of the waves must satisfy the boundary conditions imposed by the cube. The perpendicular components  $x_1, x_2$ , and  $x_3$  must have nodes at each surface of the cube (figure 2.10.1).

The wave equation in three dimensions,

$$\begin{aligned} \frac{\partial^2 u(x_1, x_2, x_3, t)}{\partial x_1^2} + \frac{\partial^2 u(x_1, x_2, x_3, t)}{\partial x_2^2} + \frac{\partial^2 u(x_1, x_2, x_3, t)}{\partial x_3^2} \\ = \frac{1}{v^2} \frac{\partial^2 u(x_1, x_2, x_3, t)}{\partial t^2}, \end{aligned} \quad (2.10.1)$$

is separated in the usual way, leading to three separation constants

$$\rho^2 + \sigma^2 + \tau^2 = \beta^2.$$

As in the two-dimensional case,  $\omega = v\beta$ . Imposition of boundary conditions on the components of the waves in three dimensions leads to

$$\omega = v\beta = v\pi \left( \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right)^{1/2} \quad (2.10.2a)$$

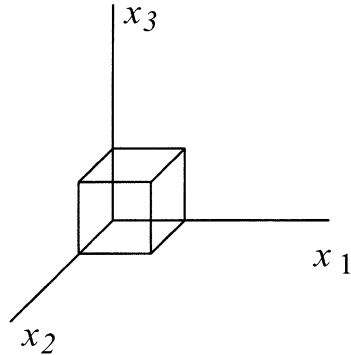


Figure 2.10.1. Each face of a cubic box establishes a nodal plane for a standing wave.

or

$$\omega = \frac{v\pi}{L} (n_1^2 + n_2^2 + n_3^2)^{1/2}, \quad (2.10.2b)$$

where  $L^2$  can be factored out because the edges of the cube are equal in length. By the Pythagorean theorem,  $(n_1^2 + n_2^2 + n_3^2)^{1/2} = n$  in a number space of  $n_1, n_2$ , and  $n_3$  measured along orthogonal Cartesian coordinates; hence

$$\omega = \frac{v\pi}{L} n. \quad (2.10.2c)$$

We shall call this space the *quantum number space* as distinct from the  $x_1, x_2, x_3$  space. If  $n_1, n_2$ , and  $n_3$  are very large,  $n$  approaches the radius of a sphere in the three-dimensional space spanned by  $n_1, n_2$ , and  $n_3$ . This fact will be useful to us very soon.

## 2.11 The Boltzmann Distribution

Originally derived on the assumption that energy is continuous, the Boltzmann distribution gives a number density  $dn/d\varepsilon$  of particles in an infinitesimal energy interval  $\varepsilon + d\varepsilon$ ,

$$\frac{dn}{d\varepsilon} = Ae^{-\varepsilon/kT}. \quad (2.11.1)$$

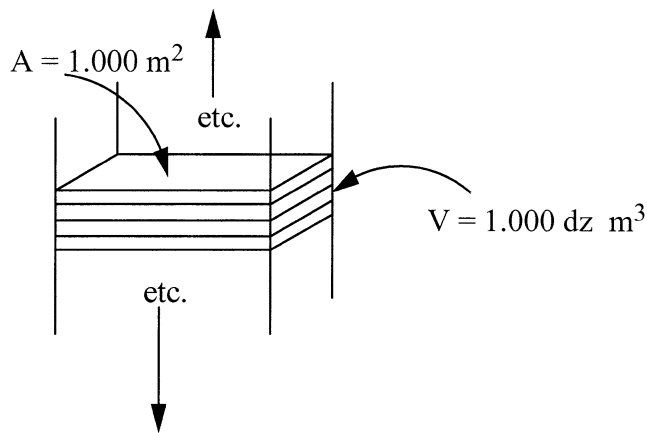


Figure 2.11.1. A column of air segmented into thin  $1.000 \text{ m}^2$  slices. The vertical dimension is  $z$ .

If, as is reasonable, we take all our infinitesimals  $d\varepsilon$  to be the same size, the proportionality constant can be made to cancel:

$$\frac{\frac{dn_1}{d\varepsilon}}{\frac{dn_0}{d\varepsilon}} = \frac{dn_1}{dn_0} = \frac{Ae^{-\varepsilon_1/kT}}{Ae^{-\varepsilon_0/kT}} = e^{-(\varepsilon_1 - \varepsilon_0)/kT}.$$

Since the zero of energy can be specified arbitrarily, let  $\varepsilon_0 = 0$  and  $\varepsilon_1 = \varepsilon$ . Now the ratio of number densities is

$$\frac{dn_1}{dn_0} = e^{-\varepsilon/kT}. \quad (2.11.2)$$

An example is the *barometric equation*, in which we consider two infinitesimal slices of a vertical column of air shown in figure 2.11.1. Pressure is force per unit area. The pressure exerted by many particles is proportional to their number because each particle makes its distinct contribution to the force. The pressure in each slice is proportional to the number density in the slice, provided that the temperature is constant along the vertical column, so that

$$\frac{p}{p_0} = e^{-mgh/kT} \quad (2.11.3)$$

where  $mgh$  is the potential energy of particles of mass  $m$  at a height  $h$  above  $h = 0$  (sea level) and  $g = 9.807 \text{ m s}^{-2}$  is the acceleration due to gravity at sea level. Because pressure is a collective effect of particle impact, the actual number of particles  $n$  in a narrow interval of altitude at  $h$  is

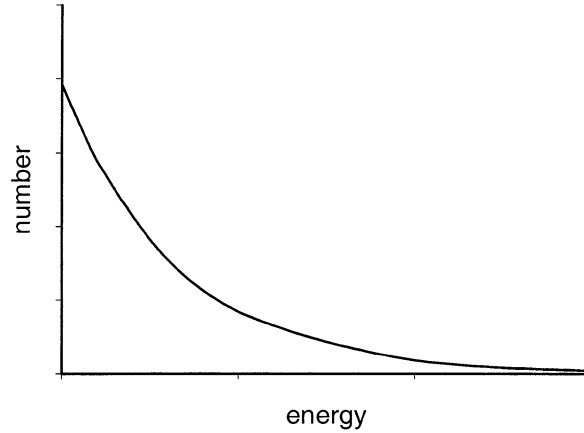


Figure 2.11.2. The Boltzmann function in  $n - \varepsilon$  space.

proportional to the number  $n_0$  in a similar interval at the defined zero  $h = 0$ ,

$$\frac{n}{n_0} = e^{-mgh/kT} \quad (2.11.4a)$$

or

$$n = n_0 e^{-mgh/kT} \quad (2.11.4b)$$

where  $k$  is Boltzmann's constant (section 2.14).

The Boltzmann distribution for continuous  $\varepsilon$  defines a curve in *number-energy space* (figure 2.11.2). If we recognize that  $n$  is a measure of pressure and  $\varepsilon$  is a measure of altitude, such a curve describes the change in atmospheric pressure with altitude (complicated by variations in  $T$ ). Just as ordinary density is weight per unit volume, say  $\text{kg m}^{-3}$ , we shall often have cause to speak of *number densities* as the number of particles per unit volume,  $n \text{ m}^{-3}$ , or, in a one-dimensional number-energy space, as the number of particles per unit of energy.

## 2.12 Degrees of Freedom

The idea of degrees of freedom is conveyed nicely by a consideration of the energy of a classical ideal gas. By definition, the potential energy of interparticle interaction in an ideal gas is negligible and the gravitational potential energy within a container is constant provided that the vertical dimension is small with respect to the radius of the earth. The only energy

of ideal gas particles is kinetic. Kinetic energy is energy of motion. Collisions in an ideal gas are elastic, so particles are free to exchange energy. In three-dimensional space (3-space), the kinetic energy of a particle can be broken up into a contribution from each dimension of the motion. For the average energy of a large number of particles, there is nothing to make us prefer one dimension over the other two. There are three *degrees of freedom* and energy is *partitioned equally* among them.

### 2.13 Kinetic Energy per Degree of Freedom

Let a mole of noninteracting particles be confined to a cubic container  $L$  on an edge. For the moment, concentrate on one particle. When a single particle with a component in the  $x$  direction collides with one of the two container walls perpendicular to the  $x$  direction, the  $x$  component of its momentum,  $p_x = mv_x$ , changes from  $p_x$  to  $-p_x$ . The total momentum change is  $2p_x$ , having a scalar magnitude of  $\tilde{p}_x = 2mv_x$ . (Note that we are using italic  $v$  for the particle speed now that there is no danger of confusing it with  $v$ .)

In order to collide a second time with the same wall, the particle must travel to the opposite wall and back again, a distance of  $2L$ . The frequency of collisions with the wall perpendicular to the  $x$  component of its motion is the  $x$  component of its speed divided by the distance it must travel:

$$\text{freq} = \frac{v_x}{2L}. \quad (2.13.1)$$

The magnitude of the force  $f$  transmitted to the wall is the momentum change per collision times the number of collisions:

$$f = 2\tilde{p}_x \frac{v_x}{2L} = 2mv_x \frac{v_x}{2L} = m \frac{v_x^2}{L}. \quad (2.13.2)$$

Pressure  $p$  is force per unit area and the area of one wall of the container is  $L^2$ ; hence

$$p = \frac{f}{L^2} = \frac{mv_x^2}{L} \left( \frac{1}{L^2} \right) = \frac{mv_x^2}{L^3} = \frac{mv_x^2}{V} \quad (2.13.3)$$

per particle, or

$$pV = mv_x^2 \quad (2.13.4)$$

per particle, where  $V = L^3$  is the volume of the container.

By Pythagoras's theorem, the length of the velocity vector is related to its components as

$$v^2 = v_x^2 + v_y^2 + v_z^2.$$

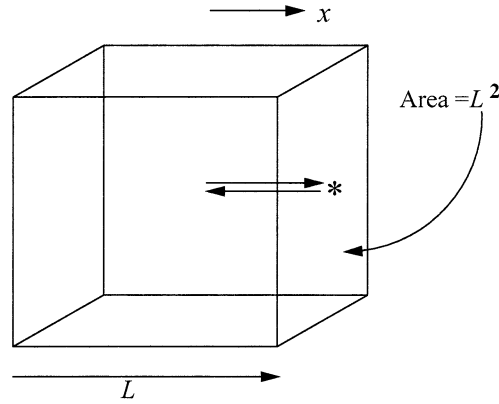


Figure 2.13.1. A gas molecule in a cubic container. Upon executing a perfectly elastic collision \* with a wall, the change in momentum is  $mv - (-mv) = 2mv$ .

The *root mean square* average of  $N$  squared speeds for a large collection of particles moving randomly in the container is defined as  $v_{\text{rms}}^2$ :

$$\frac{\sum_{i=1}^N v_i^2}{N} \equiv v_{\text{rms}}^2 \quad (2.13.5)$$

or

$$v_{\text{rms}} = \sqrt{v_{\text{rms}}^2} = \sqrt{\frac{\sum_{i=1}^N v_i^2}{N}}. \quad (2.13.6)$$

Because  $N$  is large, on average,

$$v_x^2 = v_y^2 = v_z^2.$$

Assuming free exchange of energy through particle collisions, no direction is preferred over any other, that is,

$$v_{\text{rms}}^2 = 3v_x^2$$

or

$$v_x^2 = \frac{1}{3}v_{\text{rms}}^2. \quad (2.13.7)$$

The pressure-volume product due to  $N$  molecules impacting on the right-hand wall of the cube perpendicular to the  $x$  coordinate is

$$pV = Nm v_x^2 = \frac{1}{3}Nm v_{\text{rms}}^2. \quad (2.13.8)$$

This equation gives the pressure on the other faces of the cube too, because pressure is constant within the container. Multiplying and dividing by 2 leads to

$$pV = \frac{2}{3}N \left( \frac{1}{2}mv_{\text{rms}}^2 \right) = \frac{2}{3}N \bar{\epsilon}_{\text{kin}} \quad (2.13.9)$$

where the root-mean-square kinetic energy is  $\frac{1}{2}mv_{\text{rms}}^2$  and  $\bar{\epsilon}_{\text{kin}}$  is the kinetic energy for a representative or average particle in the ensemble. For a large number of particles,  $N$ ,

$$pV = \frac{2}{3}N \bar{\epsilon}_{\text{kin}} = \frac{2}{3}\bar{E}_{\text{kin}} \quad (2.13.10)$$

where  $\bar{E}_{\text{kin}}$  is the average value of the total energy of all the particles. It turns out, from statistical arguments, that fluctuations in energy away from  $\bar{E}_{\text{kin}}$  are vanishingly small for a very large number of particles. Therefore, we drop the notation  $\bar{E}_{\text{kin}}$  and simply regard  $E_{\text{kin}}$  as the total kinetic energy. We can select the Avogadro number as the number of particles in our ensemble,  $N = N_A$ , and, since we know that  $pV = RT$  for one mole of an ideal gas, we have

$$E_{\text{kin}} = \frac{3}{2}PV = \frac{3}{2}RT \quad (2.13.11)$$

where, for  $N = N_A$ ,  $E_{\text{kin}}$  is the *molar energy in joules, J*. The important principle emerges that the *average kinetic energy per particle*  $\bar{\epsilon}_{\text{kin}}$  is  $3RT/2N_A$  or  $RT/2N_A$  *per particle per degree of freedom*.

## 2.14 Boltzmann's Constant

From

$$\bar{\epsilon}_{\text{kin}} = \frac{3}{2} \frac{R}{N_A} T \quad (2.14.1)$$

we can find the important constant

$$\frac{R}{N_A} = \frac{8.3145}{6.022 \times 10^{23}} = 1.381 \times 10^{-23} \text{ J K}^{-1} = k_B, \quad (2.14.2)$$

that is,

$$\bar{\epsilon}_{\text{kin}} = \frac{3}{2}k_B T \quad (2.14.3)$$

where  $k_B$  is the universal gas constant *per particle*. From this point on, we shall denote this constant  $k_B$ . Written in terms of  $k_B$  and equally partitioned among three degrees of freedom the *kinetic energy per degree of*

freedom is  $\frac{1}{2}k_B T$ . It is to be emphasized that everything said here derives from classical mechanics, not quantum mechanics.

## 2.15 The Translational Energy

The energy calculated in this way is frequently called the *translational energy* because it is calculated from a model consisting of point masses executing only translational motion in 3-space as distinct from extended molecular structures, which may also execute rotational or vibrational motion.

To confirm this, we can look to the experimental thermodynamics of the noble (monatomic) gases which are, to a good approximation, non-interacting particles. For a small temperature rise,

$$\frac{dE}{dT} \equiv C_V$$

where  $E$  is the molar energy and  $C_V$  is the *molar heat capacity at constant volume*. If it is true that  $E_{\text{ideal gas}} = \frac{3}{2}RT$  for one mole, then  $E = \frac{3}{2}(8.3145)T = 12.472T$  in joules, also for one mole of an ideal gas. For experimental verification, we ask whether the constant-volume molar heat capacity is  $d(12.472T)/dT = 12.472 \text{ J K}^{-1} \text{ mol}^{-1}$ . Helium and neon are examples of real gases that are very nearly ideal and that have no vibratory or rotatory modes of motion. The experimental molar heat capacities at constant volume are

$$C_V(\text{He}) = 12.471 \text{ J K}^{-1} \text{ mol}^{-1},$$

$$C_V(\text{Ne}) = 12.471 \text{ J K}^{-1} \text{ mol}^{-1},$$

giving us a very impressive confirmation of the theoretical value.

## 2.16 The Energy of a Vibrational State Is $k_B T$

We have seen that the average energy of an ideal gas confined to a cubic container is  $\frac{1}{2}k_B T$  per particle per degree of freedom. If a system of fixed harmonic oscillators is in the same cubic container along with an ideal gas, its average kinetic energy must be  $k_B T$  per degree of freedom per oscillator. If it were not, the system would not be in thermal equilibrium. The difference is that an ideal gas has three degrees of freedom, the  $x$ ,  $y$ , and  $z$  dimensions, while a harmonic oscillator has only one, along the coordinate of vibration. With only one degree of freedom, why is the energy of the harmonic oscillator  $k_B T$  rather than  $\frac{1}{2}k_B T$ ? There is only

one kind of energy in an ideal gas, kinetic energy of translation, while a harmonic oscillator has two, kinetic energy *and* potential energy of vibration. Classically, the kinetic energy and potential energy of a harmonic oscillator are equal. Each vibrational state contributes  $2(\frac{1}{2}k_B T) = k_B T$  to the energy of the system.

Boltzmann argued (in 1871) that a solid element can be regarded as  $N$  harmonic oscillators, each with three degrees of freedom,  $x$ ,  $y$ , and  $z$  in Cartesian space. Since  $N = N_A$ , the Avogadro number for a molar quantity, the molar energy  $U$  of a pure solid element should be

$$U = 3N_A k_B T = 3RT \quad (2.16.1)$$

where  $R$  is the molar gas constant,  $R = N_A k_B$ ; hence the molar heat capacity, which is the specific heat per gram times the gram atomic weight, is

$$C = \frac{\partial U}{\partial T} = 3R = 3(8.3145) = 24.9 \text{ J mol}^{-1},$$

in agreement with the law of Dulong and Petit. (Where an unsubscripted  $C$  is used to denote the specific heat, constant volume should be assumed.)

## 2.17 Trouble Brewing

The preceding arguments assume that the oscillator is fixed to a lattice site in a crystal. If a diatomic molecule, which is free to move within a container, also executes harmonic motion along its bond axis, its energy is translational *and* vibrational,  $3(\frac{1}{2}k_B T) + 2(\frac{1}{2}k_B T) = \frac{5}{2}k_B T$  per molecule. The expected molar heat capacity,  $\frac{5}{2}R = \frac{5}{2}(8.1345) = 20.79 \text{ J K}^{-1} \text{ mol}^{-1}$ , is found near room temperature for some diatomic molecules in the gaseous state, but not for others:

$$\begin{aligned} C_V(\text{N}_2) &= 20.79 \text{ J K}^{-1} \text{ mol}^{-1}, \\ C_V(\text{O}_2) &= 21.04 \text{ J K}^{-1} \text{ mol}^{-1}, \\ C_V(\text{F}_2) &= 22.99 \text{ J K}^{-1} \text{ mol}^{-1}. \end{aligned}$$

One can rationalize a heat capacity that is higher than  $20.81 \text{ J K}^{-1} \text{ mol}^{-1}$  by invoking the idea that a diatomic molecule rotates about its center of gravity, but addition of a “little bit” to the molar heat capacity violates the rule of  $\frac{1}{2}k_B T$  per degree of freedom. *This is a serious problem for classical physics.* We shall see that the problem of anomalous low-temperature heat capacities of crystals is similar to the problem of anomalous heat capacities of diatomic molecules, and when we have the solution to one problem, we shall have the solution to the other.

## PROBLEMS

- 2.1. Show that  $x = Ae^{i\omega t}$  is a solution of (satisfies) the Newton-Hooke equation, equation 2.1.3.
- 2.2. Show that the sum of solutions

$$x = A \sin \omega t + B \cos \omega t$$

is a solution to the Newton-Hooke equation.

- 2.3. Referring to figure 2.1.2, how do we know that at  $t = 0$ ,  $\dot{x} = 0$  for curve Q?
- 2.4. Taking  $m = 1.00$  kg, the displacement in figure 2.1.2 in meters, and  $k = 1.00 \text{ N m}^{-1}$  ( $\omega = 1.00 \text{ s}^{-1}$ ), what are the initial potential energies for the mass if it is to follow trajectories P, Q, and R?
- 2.5. Given the conditions in problem 2.4, find the initial speed of the 1.00 kg mass starting out on trajectories P, Q, and R in figure 2.1.2, that is, verify the last sentence in the caption of figure 2.1.2. The maximum excursion of trajectory R is 0.250 m.
- 2.6. Sketch the normal modes of vibration of a square membrane analogous to figure 2.9.1 for  $\{n_1 = 1, n_2 = 1\}$ ,  $\{n_1 = 1, n_2 = 2\}$ ,  $\{n_1 = 2, n_2 = 1\}$ ,  $\{n_1 = 2, n_2 = 2\}$ ,  $\{n_1 = 1, n_2 = 3\}$ ,  $\{n_1 = 3, n_2 = 1\}$ ,  $\{n_1 = 3, n_2 = 3\}$ . Which are degenerate?
- 2.7. A 2.00 kg mass is suspended from a fixed point by a 6.00 m length of 2.00 mm diameter copper wire. A slight “ping” is struck with a mallet near the fixed end, causing a transverse wave to travel down the wire. How long does it take the wave to get to the 2.00 kg mass? The density of copper is  $8920 \text{ kg m}^{-3}$ .