For an ideal monatomic gas the *entire* energy is kinetic, so that the mean energy per mole of gas is simply

$$\bar{E} = N_a(\tfrac{3}{2}kT) = \tfrac{3}{2}RT$$

The molar specific heat at constant volume is then

$$c_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = \frac{3}{2}R \qquad (7\cdot 6\cdot 3)$$

Brownian motion Consider a macroscopic particle of mass m immersed in a liquid at temperature T. Let the z axis point in the direction of the gravitational field (if one is present) and focus attention on v_x, the x component of the center-of-mass velocity of the particle. The mean value of v_x must vanish by symmetry; i.e.,

$$\bar{v}_x = 0$$

But it is, of course, not true that v_x itself is always found to vanish if one observes a collection of such particles; velocity fluctuations *do* occur. Indeed, the equipartition theorem can be applied to the center-of-mass energy terms just as in the preceding example; thus one can conclude that

$$\overline{\tfrac{1}{2}mv_x^2} = \tfrac{1}{2}kT \qquad \text{or} \qquad \overline{v_x^2} = \frac{kT}{m}$$

The dispersion v_x^2 in this velocity component is thus negligibly small when m is large. For example, when the particle is the size of a golf ball, fluctuations in its velocity are essentially unobservable and the particle appears to be at rest. But when m is small (e.g., when the particle has a diameter of about a micron), $\overline{v_x^2}$ becomes appreciable and velocity fluctuations can readily be observed under a microscope. The fact that small particles of this kind perpetually move about in a random manner was first observed by Brown, a botanist, in the last century. The phenomenon is, therefore, called "Brownian motion." It was explained theoretically by Einstein in 1905 on the basis of the intrinsic thermal fluctuations resulting from the interaction of the small particle with the heat bath, i.e., from the random collisions of the particle with the molecules of the liquid. The phenomenon was historically important in helping to gain acceptance for the atomic theory of all matter and for the validity of the statistical description thereof.

Harmonic oscillator Consider a one-dimensional harmonic oscillator which is in equilibrium with a heat reservoir at absolute temperature T. The energy of such an oscillator is given by

$$E = \frac{p^2}{2m} + \frac{1}{2}\kappa_0 x^2 \qquad (7\cdot 6\cdot 4)$$

where the first term on the right is the kinetic energy involving the momentum p and mass m, and the second term on the right is the potential energy involving the position coordinate x and spring constant κ_0. Each of these terms is quadratic in the respective variable. Hence the equipartition theorem leads immediately to the following conclusions, valid in the classical approximation:*

$$\text{mean kinetic energy} = \frac{1}{2m}\overline{p^2} = \tfrac{1}{2}kT$$

$$\text{mean potential energy} = \tfrac{1}{2}\kappa_0\overline{x^2} = \tfrac{1}{2}kT$$

Hence the mean total energy is

$$\bar{E} = \tfrac{1}{2}kT + \tfrac{1}{2}kT = kT \tag{7·6·5}$$

It is instructive to treat this example by quantum mechanics as an illustration of the limits of validity of the classical description. According to quantum mechanics the possible energy levels of the harmonic oscillator are given by

$$E_n = (n + \tfrac{1}{2})\hbar\omega \tag{7·6·6}$$

where the possible states of the oscillator are labeled by the quantum number n which can assume all integral values

$$n = 0, 1, 2, 3, \ldots$$

Here $\hbar$ is Planck's constant (divided by 2π) and

$$\omega = \sqrt{\frac{\kappa_0}{m}} \tag{7·6·7}$$

is the classical angular frequency of oscillation of the oscillator. The mean energy of the oscillator is then given by

$$\bar{E} = \frac{\sum_{n=0}^{\infty} e^{-\beta E_n}E_n}{\sum_{n=0}^{\infty} e^{-\beta E_n}} = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{\partial}{\partial\beta}\ln Z \tag{7·6·8}$$

where $$Z \equiv \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\beta\hbar\omega} \tag{7·6·9}$$

or $$Z = e^{-\frac{1}{2}\beta\hbar\omega}\sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} = e^{-\frac{1}{2}\beta\hbar\omega}(1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \cdots)$$

This sum is just an infinite geometric series where each term is obtained from the preceding one as a result of multiplication by $e^{-\beta\hbar\omega}$. The sum can thus immediately be evaluated to give

$$Z = e^{-\frac{1}{2}\beta\hbar\omega}\frac{1}{1 - e^{-\beta\hbar\omega}} \tag{7·6·10}$$

or $$\ln Z = -\tfrac{1}{2}\beta\hbar\omega - \ln(1 - e^{-\beta\hbar\omega}) \tag{7·6·11}$$

Thus one obtains, by (7·6·8),

$$\bar{E} = -\frac{\partial}{\partial\beta}\ln Z = -\left(-\frac{1}{2}\hbar\omega - \frac{e^{-\beta\hbar\omega}\hbar\omega}{1 - e^{-\beta\hbar\omega}}\right)$$

or

$$\blacktriangleright \qquad \bar{E} = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right) \tag{7·6·12}$$

Let us now investigate some limiting cases. When

$$\beta\hbar\omega = \frac{\hbar\omega}{kT} \ll 1 \tag{7·6·13}$$

the temperature is so high that the thermal energy kT is large compared to the separation $\hbar\omega$ between energy levels. Then one expects the classical description to be a good approximation. Indeed, if (7·6·13) is valid, the exponential function can be expanded in Taylor's series so that (7·6·12) becomes

$$\bar{E} = \hbar\omega\left[\frac{1}{2} + \frac{1}{(1 + \beta\hbar\omega + \cdots) - 1}\right] \approx \hbar\omega\left[\frac{1}{2} + \frac{1}{\beta\hbar\omega}\right]$$

$$\approx \hbar\omega\left[\frac{1}{\beta\hbar\omega}\right] \qquad \text{by virtue of (7·6·13)}$$

or

$$\bar{E} = \frac{1}{\beta} = kT \tag{7·6·14}$$

in agreement with the classical result (7·6·5).

On the other hand, at low temperatures where

$$\beta\hbar\omega = \frac{\hbar\omega}{kT} \gg 1 \tag{7·6·15}$$

one has $e^{\beta\hbar\omega} \gg 1$, so that (7·6·12) becomes

$$\bar{E} = \hbar\omega(\tfrac{1}{2} + e^{-\beta\hbar\omega}) \tag{7·6·16}$$

This is quite different from the equipartition result (7·6·5) and approaches properly the ("zero point") energy $\frac{1}{2}\hbar\omega$ of the ground state as $T \to 0$.

7 · 7 *Specific heats of solids*

Consider any simple solid with Avogadro's number N_a of atoms per mole. Examples might be copper, gold, aluminum, or diamond. These atoms are free to vibrate about their equilibirum positions. (Such vibrations are called "lattice vibrations.") Each atom is specified by three position coordinates and three momentum coordinates. Since the vibrations are supposed to be small, the potential energy of interaction between atoms can be expanded about their equilibrium positions and is therefore quadratic in the atomic displacements from their equilibrium positions. The net result is that the total energy of lattice vibrations can be written (when expressed in terms of appropriate "normal mode coordinates") in the simple form

$$E = \sum_{i=1}^{3N_a}\left(\frac{p_i^2}{2m} + \frac{1}{2}\kappa_i q_i^2\right) \tag{7·7·1}$$

Here the first term is the total kinetic energy involving the $3N_a$ (normal-mode) momenta of the atoms, while the second term is the total potential energy involving their $3N_a$ (normal-mode) coordinates. The coefficients κ_i are positive constants. Thus the total energy is the same as that of $3N_a$ independent one-dimensional harmonic oscillators. If the temperature T is high enough so that classical mechanics is applicable (and room temperature is usually sufficiently high for that), application of the equipartition theorem allows one to conclude immediately that the total mean energy per mole is

$$\bar{E} = 3N_a[(\tfrac{1}{2}kT) \times 2]$$

or

$$\bar{E} = 3N_akT = 3RT \tag{7·7·2}$$

Thus the molar specific heat at constant volume becomes

▶ $$c_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = 3R \tag{7·7·3}$$

This result asserts that at sufficiently high temperatures all simple solids have the same molar specific heat equal to $3R$ (25 joules mole^{-1} deg^{-1}). Historically, the validity of this result was first discovered empirically and is known as the law of Dulong and Petit. Table 7·7·1 lists directly measured values of the molar specific heat c_p at constant *pressure* for some solids at room temperature. The molar specific heat c_V at constant volume is somewhat less (by about 5 percent, as calculated in the numerical example of Sec. 5·7).

***Table 7 · 7 · 1** Values* of c_p (joules mole^{-1} deg^{-1}) for some solids at T = 298°K*

Solid	c_p	*Solid*	c_p
Copper	24.5	Aluminum	24.4
Silver	25.5	Tin (white)	26.4
Lead	26.4	Sulfur (rhombic)	22.4
Zinc	25.4	Carbon (diamond)	6.1

* "American Institute of Physics Handbook," 2d ed., McGraw-Hill Book Company, New York, 1963, p. 4–48.

Of course, the preceding arguments are not valid for solids at appreciably lower temperatures. Indeed, the third law leads to the general result (5·7·19), which requires that c_V must approach zero as $T \rightarrow 0$. One can obtain an approximate idea of the behavior of c_V at all temperatures by making the crude assumption (first introduced by Einstein) that all atoms in the solid vibrate with the *same* angular frequency ω. Then $\kappa_i = m\omega^2$ for all terms i in (7·7·1), and the mole of solid is equivalent to an assembly of $3N_a$ independent one-dimensional harmonic oscillators. These can be treated by quantum mechanics so that their total mean energy is just $3N_a$ times that of the single oscillator discussed in (7·6·12); i.e.,

$$\bar{E} = 3N_a\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right) \tag{7·7·4}$$

Hence the molar specific heat of the solid on the basis of this simple Einstein model is given by

$$c_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial \beta}\right)_V \frac{\partial \beta}{\partial T} = -\frac{1}{kT^2}\left(\frac{\partial \bar{E}}{\partial \beta}\right)_V$$

$$= -\frac{3N_a\hbar\omega}{kT^2}\left[-\frac{e^{\beta\hbar\omega}\hbar\omega}{(e^{\beta\hbar\omega}-1)^2}\right]$$

or

$$c_V = 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T}-1)^2} \tag{7·7·5}$$

where $R \equiv N_a k$ and where we have written

$$\beta\hbar\omega = \frac{\hbar\omega}{kT} \equiv \frac{\Theta_E}{T}$$

by introducing the characteristic "Einstein temperature"

$$\Theta_E \equiv \frac{\hbar\omega}{k} \tag{7·7·6}$$

If the temperature is so high that $kT \gg \hbar\omega$ or $T \gg \Theta_E$, then $\Theta_E/T \ll 1$ and expansion of the exponentials in (7·7·5) yields again the classical result

$$\text{for } T \gg \Theta_E, \qquad c_V \to 3R \tag{7·7·7}$$

On the other hand, if the temperature is so low that $kT \ll \hbar\omega$ or $T \ll \Theta_E$ then $\Theta_E/T \gg 1$ and the exponential factor becomes very large compared to unity. The specific heat then becomes quite small; more precisely,

$$\text{for } T \ll \Theta_E, \qquad c_V \to 3R\left(\frac{\Theta_E}{T}\right)^2 e^{-\Theta_E/T} \tag{7·7·8}$$

Thus the specific heat should approach zero exponentially as $T \to 0$. Experimentally the specific heat approaches zero more slowly than this, indeed $c_V \propto T^3$ as $T \to 0$. The reason for this discrepancy is the crude assumption that all atoms vibrate with the same characteristic frequency. In reality this is, of course, not the case (even if all the atoms are identical). The reason is that each atom does not vibrate separately as though it were experiencing a force due to stationary neighboring atoms; instead, there exist many different modes of motion in which various *groups* of atoms oscillate in phase at the same frequency. It is thus necessary to know the many different possible frequencies of these modes of oscillation (i.e., the values of all the coefficients κ_i in (7·7·1)). This problem will be considered in greater detail in Secs. 10·1 and 10·2. But it is qualitatively clear that, although T may be quite small, there are always some modes of oscillation (those corresponding to sufficiently large groups of atoms moving together) with a frequency ω so low that $\hbar\omega \ll kT$. These modes still contribute appreciably to the specific heat and thus prevent c_V from decreasing quite as rapidly as indicated by (7·7·8).

Nevertheless, the very simple Einstein approximation does give a reasonably good description of the specific heats of solids. It also makes clear the existence of a characteristic parameter Θ_E which depends on the properties of

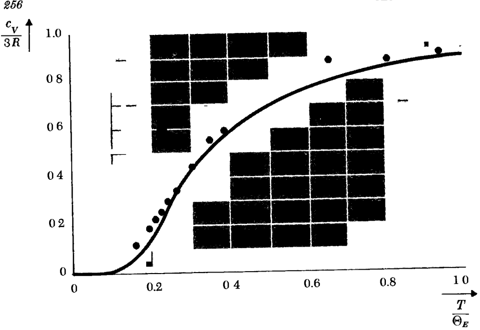

Fig. 7·7·1 ***Temperature dependence of*** c_V ***according to the Einstein model. The points are experimental values of*** c_V ***for diamond, the fit to the curve being achieved by choosing*** $\Theta_E = 1320°K$ ***(after A. Einstein, Ann. Physik, vol. 22, p. 186 (1907)).***

the solid under consideration. For example, if a solid has atoms of low molecular weight and is hard (i.e., relatively incompressible), this implies that each oscillator has a small mass m and a large spring constant κ_0 (i.e., the spring is stiff). Then (7·6·7) shows that the angular frequency of vibration ω of the atoms is large, or that Θ_E defined in (7·7·6) is large. Thus one must go to higher temperatures before the classical limit $c_V = 3R$ is reached. This explains why a solid such as diamond, which consists of relatively light carbon atoms and is quite hard, has at room temperature a specific heat c_V which is still considerably smaller than the classical value $3R$ (see Table 7·7·1). Thus for diamond a reasonably good fit with experiment can be obtained by choosing $\Theta_E = 1320°K$ (see Fig. 7·7·1). For most other solids Θ_E lies closer to $\Theta_E \approx 300°K$. This corresponds to a frequency of vibration $\omega/2\pi \approx k\Theta_E/(2\pi\hbar)$ of about 6×10^{12} cycles/sec, i.e., to a frequency in the infrared region of the electromagnetic spectrum.

Before the introduction of quantum ideas it was not possible to understand why the molar specific heats of solids should fall below the classical equipartition value $3R$ at low temperatures. In 1907 Einstein's theory clarified the mystery and helped to gain acceptance for the new quantum concepts.