

# Maxwellian speed distribution of a gas

## A1.1 Introduction

In this appendix we will work out the distribution of molecular speeds in a gas by explicitly calculating three functions that describe the properties of dilute gases. These are:

- The *density of states function*  $g(E)dE$ , which yields the number of quantum states with energies between  $E$  and  $dE$ .
- The *occupation function*  $f(E,T)$ , which yields the average number of particles occupying a single quantum state with energy  $E$  and temperature  $T$ .
- The *distribution function*  $D(E,T)$ , which is the product  $f(E,T)g(E)dE$  and yields the average

number of particles occupying quantum states with energies between  $E$  and  $dE$  at temperature  $T$ .

Once we have worked out the distribution function, we will be able to state *on average* how many molecules in a gas have energies between  $E$  and  $E + dE$ . Then, since we know that for simple molecules the energy of a molecule is entirely kinetic ( $E = \frac{1}{2}mv^2$ ), we can deduce how many molecules have speeds between  $v$  and  $v + dv$ . In what follows we consider only the properties of simple molecules of mass  $m$  and no internal degrees of freedom.

## A1.2 The density of states function

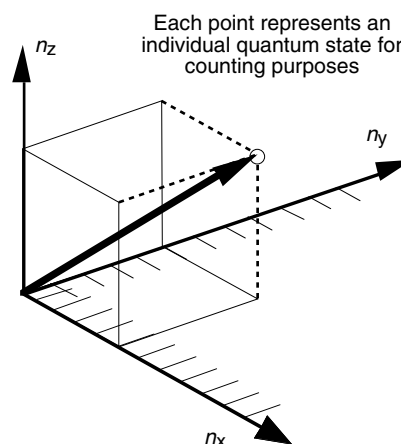
Our determination of the density of states function is based on an analysis of the ‘particle in a box’ problem (§2.4.3 and §6.5.2). That is, we think of molecules of gas as occupying the quantum states of a ‘particle in a box’. In §6.5 we considered this problem for the case of electrons packed densely together inside a metal, but now we consider the case of molecules packed at low density into an empty box. The first step is to develop a way of systematically counting the quantum states of a ‘particle in a box’ (Figure A1.1). We will consider two counting techniques: a simple way and a more complicated way. We will, of course, choose the more complicated way.

### The quantum states: standing waves

The first method of counting is derived from Equation 2.49 for the energies of allowed quantum states:

$$E(n_x, n_y, n_z) = \frac{h^2}{8mL^2} [n_x^2 + n_y^2 + n_z^2] \quad (\text{A1.1})$$

**Figure A1.1** A scheme for counting quantum states in the ‘particle in a box’ problem when lots of particles are present. Each quantum state is represented by a point on an  $n_x, n_y, n_z$  graph. The energy of the state is proportional to the square of its distance from the origin on this graph. For this reason, the occupied quantum states cluster in a quadrant of a sphere around the origin



We represent an allowed quantum state by a point on a three-dimensional graph whose axes are  $n_x$ ,  $n_y$ , and  $n_z$  respectively. Thus each individual quantum state is represented by a single point on the graph, and the points representing the quantum states are distributed uniformly on a ‘mesh’ throughout the graph. Because of this, by measuring ‘volumes’ on this three-dimensional graph we can – with a fair degree of approximation – also count quantum states. Further, we can also simply state that the energy of a particular state is given by  $h^2/8mL^2 \times$  [the square of the length of the vector from the origin to the point representing that quantum state](Figure A1.1).

However in order to develop the ‘geometrical’ method of counting quantum states further, we will change to a second view of the quantum states of a particle in a box.

### The quantum states: travelling waves

The second method of counting arises from a re-consideration of the particle in a box problem. We will arrive at similar, but distinctly different, solutions to the Schrödinger equation: travelling wave solutions.

In §2.3.3 we required the wave functions to be zero at the edge of the box because we imagined the edge of the box to represent the walls of the box. We supposed that molecules were not allowed to penetrate the walls (otherwise they are not walls!) and so the wave functions of the particles must be zero there. Now, however, we consider a more complex situation. We imagine a volume of the gas which is *representative* of the gas as a whole and we imagine it to be surrounded by *identical volumes* of gas. The differences between this situation and the standing wave situation are illustrated in Figure A1.2. You may consider this to be ‘trickery’, and it is. It is a mathematical trick, but it will allow us to see more clearly the physics of what is happening in the gas.

The key difference to the problem is that now instead of requiring that the wave functions be zero at the edges of the box, i.e.  $\Psi(-x/2) = \Psi(+x/2) = 0$ , we require that the wave functions be identical in neighbouring boxes, i.e.

$$\Psi(x) = \Psi(x + L_x) \quad (\text{A1.2})$$

where  $L_x$  is the length of the box under consideration. If the solutions are  $\sin(kx)$  or  $\cos(kx)$  waves this is equivalent to requiring that:

$$\cos(k_x x) = \cos(k_x [x + L_x])$$

or (A1.3)

$$\sin(k_x x) = \sin(k_x [x + L_x])$$

The requirements A1.3 are known as *Born–von Karmen boundary conditions*, and lead to only discrete values of  $k$  being allowed solutions. Let us follow one of Equations A1.3 through explicitly to find these conditions for  $k_x$ . The boundary conditions require that:

$$\cos(k_x x) = \cos(k_x [x + L_x]) = \cos(k_x x + k_x L_x) \quad (\text{A1.4})$$

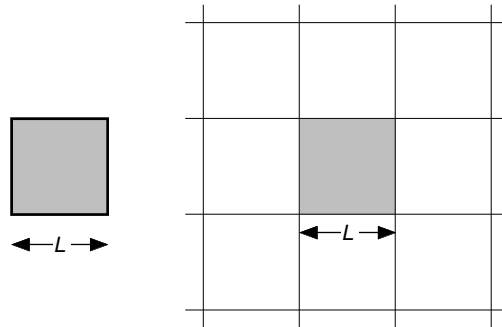
Using the trigonometric identity:

$$\cos(A+B) = \cos A \cos B - \sin A \sin B \quad (\text{A1.5})$$

Equation A1.4 can be rewritten as:

$$\cos(k_x x) = \cos(k_x x) \cos(k_x L_x) - \sin(k_x x) \sin(k_x L_x) \quad (\text{A1.6})$$

**Figure A1.2** Illustration of two approaches to the particle in a box problem. (a) The first approach uses the idea of an isolated box representing the entire crystal. The second approach (b) uses the idea of a box of representative material surrounded by identical copies of itself. The edges of the actual crystal are imagined to be far enough away that they do not significantly affect the particles deep inside the box.



Clearly, in general this equation is not true! It is only true when  $\cos(k_x L_x) = 1$  and when the second term is zero. Since  $x$  can vary, this will only be true when  $\sin(k_x L_x) = 0$ . Now  $\cos(k_x L_x) = 1$  when  $k_x L_x = 0, \pm 2\pi, \pm 4\pi, \dots$  etc, and these values of  $k_x L_x$  also cause  $\sin(k_x L_x)$  to be zero. So the Born-von Karmen boundary conditions are satisfied when:

$$k_x L_x = 0, \pm 2\pi, \pm 4\pi, \dots \quad (\text{A1.7})$$

i.e. when:

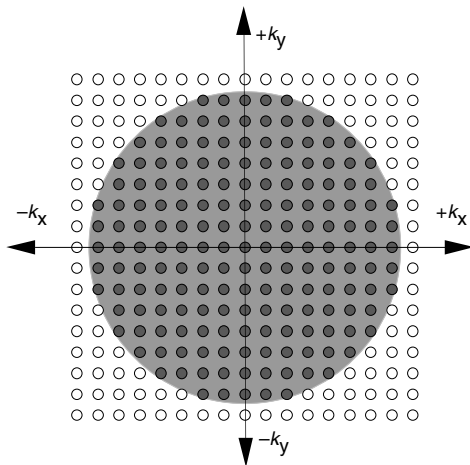
$$k_x = 0, \frac{\pm 2\pi}{L_x}, \frac{\pm 4\pi}{L_x}, \dots \quad (\text{A1.8})$$

or in general when:

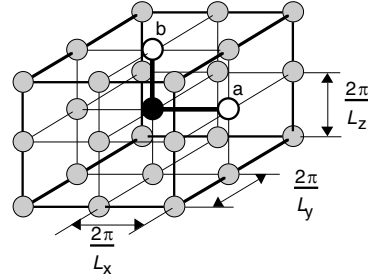
$$k_x = \frac{2m_x\pi}{L_x} \text{ where } m_x = 0, \pm 1, \pm 2, \dots \quad (\text{A1.9})$$

I shall leave it to you to show that following the second of Equations A1.3 through in a similar way [using  $\sin(A + B) = \sin A \cos B + \cos A \sin B$ ] results in exactly the same conclusion.

**Figure A1.3** A cross-section through 'k-space'. Each small circle represents an allowed travelling wave solution to the Schrödinger equation. The filled (unfilled) circles represent occupied quantum states which are occupied (unoccupied). The configuration of occupied and unoccupied states shown is similar to that expected in a metal at absolute zero. Only the lowest energy states (low  $k$  = long wavelength = low energy) are occupied. In three dimensions the occupied states form a sphere in  $k$ -space known as the *Fermi sphere*.



**Figure A1.4** Close up view of 'k-space'. The circles represent allowed values of  $\mathbf{k}$ . If the central point represents a solution of the Schrödinger equation with a particular value of  $k_x, k_y, k_z$ , then point  $a$  represents a solution with  $k_x$  component increased by  $2\pi/L_x$ . Similarly point  $b$  represents a solution with  $k_z$  component increased by  $2\pi/L_z$ .



We can now make sketches analogous to Figure A1.1 for this new situation. In these sketches we plot points representing  $k_x, k_y$  and  $k_z$ , which serve to label individual quantum states. The main difference between this and the  $(n_x, n_y, n_z)$  representation discussed previously is that each allowed point in space now represents a travelling wave rather a standing wave. Hence we can have negative  $k$  values and so the quantum states are distributed all around the origin rather than being confined to the positive  $|\mathbf{k}|$  octant (contrast Figures A1.1 and A1.3).

We know further that the allowed states are distributed uniformly through  $k$ -space so that if we consider a 'volume' of  $k$ -space we can work out how many allowed quantum states it contains. A close up view of our  $k$ -space graph is shown in Figure A1.4

It is clear from the Figure A1.4 that each state has around it a 'volume of  $k$ -space'  $\Delta\Omega$  given by:

$$\Delta\Omega = \frac{2\pi}{L_x} \times \frac{2\pi}{L_y} \times \frac{2\pi}{L_z} \quad (\text{A1.10})$$

and since  $L_x L_y L_z = V$  this reduces to:

$$\Delta\Omega = \frac{8\pi^3}{V} \quad (\text{A1.11})$$

This simple result embodied in Equation A1.11 is crucial. As we shall see, it enables us to count quantum states, and in particular, it enables us to

answer the following question: how many quantum states are there with wave vectors between  $k$  and  $k + dk$  ?

### How many quantum states are there with wave vectors between $k$ and $k + dk$ ?

All the quantum states with  $k$  vectors in this range correspond to points in a spherical shell of radius  $k$  and thickness  $dk$ . We can write down the ‘volume’ on the  $k$ -space graph that these points occupy as:

$$d\Omega = 4\pi k^2 dk \quad (\text{A1.12})$$

and since each point occupies a volume  $\Delta\Omega = 8\pi^3/V$  the number of quantum states  $dN$  in this shell is given by:

$$dN = \frac{4\pi k^2 dk}{8\pi^3/V} = \frac{Vk^2 dk}{2\pi^2} \quad (\text{A1.13})$$

### How many quantum states are there with energy between $E$ and $E + dE$ ?

In order to answer this we need to rewrite Equation A1.13 replacing references to  $k$  – in this case  $k^2$  and  $dk$  – with references to  $E$ . We start with:

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad (\text{A1.14})$$

We see that:

$$k^2 = \frac{2mE}{\hbar^2} \quad (\text{A1.15})$$

Differentiating Equation A1.14 we find:

$$dE = \frac{\hbar^2 k}{m} dk \quad (\text{A1.16})$$

and replacing the reference to  $k$  :

$$dE = \frac{\hbar^2 \sqrt{2mE/\hbar^2}}{m} dk \quad (\text{A1.17})$$

we arrive at:

$$dk = \frac{m}{\hbar^2 \sqrt{2mE/\hbar^2}} dE \quad (\text{A1.18})$$

We can now replace both the references to  $k$  in Equation A1.19 with references to  $E$ :

$$dN = \frac{V}{2\pi^2} \times \frac{2mE}{\hbar^2} \times \frac{m}{\hbar^2 \sqrt{2mE/\hbar^2}} dE \quad (\text{A1.19})$$

which simplifies to:

$$dN = \frac{Vm^{3/2}}{\sqrt{2\pi^2\hbar^3}} E^{1/2} dE \quad (\text{A1.20})$$

This expression is for the number of quantum states  $dN$  with energies between  $E$  and  $E + dE$ , which is exactly the definition of the density of states function  $g(E)$ . So we now have the expression we desire:

$$g(E) = \frac{dN}{dE} = \frac{Vm^{3/2}}{\sqrt{2\pi^2\hbar^3}} E^{1/2} \quad (\text{A1.21})$$

## A1.3 The occupation function

We now have to consider whether the particles which will occupy the box will be bosons or fermions. Molecules are composed of many atoms and atoms are composed of protons, neutrons and electrons. Whether a molecule is a boson or a fermion depends on way in which the spins of the component particles add together. For example, helium atoms occur in two isotopes: the rare  ${}^3\text{He}$

and the more common  ${}^4\text{He}$ .  ${}^3\text{He}$  has 2 electrons, 2 protons, and 1 neutron, all with spin  $\frac{1}{2}\hbar$ . No matter which way these are added together, the net result is always half an odd integer times  $\hbar$  and so  ${}^3\text{He}$  atoms are fermions: they obey the exclusion principle and are described by Fermi–Dirac statistics. In contrast  ${}^4\text{He}$  has 2 electrons, 2 protons and 2 neutrons which always add together to yield a

spin of zero or an integer multiple  $\hbar$ . Thus  ${}^4\text{He}$  atoms are bosons: they do *not* obey the exclusion principle, and they are described by Bose–Einstein statistics.

However, at the low densities present in gases, both fermion and boson occupation functions are well approximated by the Boltzmann occupation function. Only when the density of the gas is such that the probability of multiple occupation of quantum states becomes significant can we distinguish between the two occupation functions. However this high density regime does not occur until we reach temperatures of a few kelvin, and densities similar to those in solids and liquids.

### The Boltzmann occupation function

Independent of whether the molecules of the gas are fermions or bosons we may write the occupation function – the average occupancy of an individual quantum state – as:

$$f(E, T) = \frac{1}{\exp\left[\frac{E - \mu}{k_B T}\right] \pm 1} \quad (\text{A1.22})$$

where the upper sign corresponds to fermions and the lower sign corresponds to bosons (Equations 2.61 and 2.62). The energy  $\mu$  is known as the *chemical potential*, but is sometimes referred to as the Fermi energy when dealing with fermions. Now we could proceed to evaluate the distribution function using Equation A1.22 directly. However, there is a useful approximation that may be made when the average occupancy of a quantum state is low. As mentioned in §2.5.5, when there is little chance of two particles occupying the same quantum state, the occupation functions of fermions and bosons must be similar since they have an essentially unrestricted choice of quantum states. Thus in the low-density (classical) limit of Equation A1.22 we always have:

$$f(E, T) \ll 1 \quad (\text{A1.23})$$

If this is true, then the denominator of Equation A1.22 must be much larger than unity, which implies that:

$$\exp\left[\frac{E - \mu}{k_B T}\right] \gg 1 \quad (\text{A1.24})$$

This being so, we may write:

$$f(E, T) \approx \exp\left[-\left(\frac{E - \mu}{k_B T}\right)\right] \quad (\text{A1.25})$$

which may be factorised as:

$$f(E, T) \approx \exp\left[\frac{+\mu}{k_B T}\right] \exp\left[\frac{-E}{k_B T}\right] \quad (\text{A1.26})$$

Now the chemical potential  $\mu$  has not yet been determined, but we will be able to determine it if we notice that the average occupancy of a quantum state, when summed over all quantum states, must sum to  $N$ , the total number of particles, i.e.

$$N = \sum_{\substack{\text{All} \\ \text{quantum} \\ \text{states } i}} f(E_i, T) \approx \sum_{\substack{\text{All} \\ \text{quantum} \\ \text{states } i}} \exp\left[\frac{+\mu}{k_B T}\right] \exp\left[\frac{-E_i}{k_B T}\right] \quad (\text{A1.27})$$

We can now factor out  $\exp[+\mu/k_B T]$ , which is common to all terms in the sum:

$$N = \exp\left[\frac{+\mu}{k_B T}\right] \sum_{\substack{\text{All} \\ \text{quantum} \\ \text{states } i}} \exp\left[\frac{-E_i}{k_B T}\right] \quad (\text{A1.28})$$

and rearrange to solve for  $\exp[+\mu/k_B T]$ :

$$\exp\left[\frac{+\mu}{k_B T}\right] = \frac{N}{\sum_{\substack{\text{All} \\ \text{quantum} \\ \text{states } i}} \exp\left[\frac{-E_i}{k_B T}\right]} \quad (\text{A1.29})$$

We can now substitute this expression for  $\exp[+\mu/k_B T]$  back into Equation A1.26 to yield the desired expression for  $f(E, T)$ :

$$f(E, T) = \frac{N \exp\left[\frac{-E}{k_B T}\right]}{\sum_{\substack{\text{All} \\ \text{quantum} \\ \text{states } i}} \exp\left[\frac{-E_i}{k_B T}\right]} \quad (\text{A1.30})$$

Finally, we note that at a given temperature, both the denominator and  $N$  are constant so:

$$f(E, T) = A \exp\left[\frac{-E}{k_B T}\right] \quad (\text{A1.31})$$

which is the classical Boltzmann occupation function, Equation 2.72.

## A1.4 The distribution function

Multiplying together Equations A1.21 for the number of quantum states between energies  $E$  and  $E + dE$ :

$$dN = \frac{Vm^{3/2}}{\sqrt{2\pi^2\hbar^3}} E^{1/2} dE \quad (\text{A1.21}^*)$$

and Equation A1.31 for the average occupancy of a quantum state:

$$f(E, T) \approx A \exp\left[\frac{-E}{k_B T}\right] \quad (\text{A1.31}^*)$$

we arrive at the arrive at the *distribution function*. This tells us the average number of *particles* which occupy quantum states with energies between  $E$  and  $E + dE$ :

$$dN = A \frac{Vm^{3/2}}{\sqrt{2\pi^2\hbar^3}} E^{1/2} \exp\left[\frac{-E}{k_B T}\right] dE \quad (\text{A1.32})$$

In order to evaluate this expression for  $dN$  we need to work out a way of eliminating the undefined constant  $A$  in Equation A1.32. We can do this by integrating Equation A1.32 to find an expression for  $N$ , the total number of particles:

$$\int_{E=0}^{E=\infty} dN = N = \int_{E=0}^{E=\infty} A \frac{Vm^{3/2}}{\sqrt{2\pi^2\hbar^3}} E^{1/2} \exp\left[\frac{-E}{k_B T}\right] dE \quad (\text{A1.33})$$

Taking the constants outside of the integral we arrive at:

$$N = A \frac{Vm^{3/2}}{\sqrt{2\pi^2\hbar^3}} \int_{E=0}^{E=\infty} E^{1/2} \exp\left[\frac{-E}{k_B T}\right] dE \quad (\text{A1.34})$$

The integral is (fortunately) a standard integral which evaluates (using MathCAD or a Maths reference book) to:

$$\int_{x=0}^{x=\infty} x^{1/2} e^{-x/a} dx = \frac{\sqrt{\pi a^3}}{2} \quad (\text{A1.35})$$

where we have substituted  $x = E$  and  $a = k_B T$ . With these substitutions Equation A1.34 becomes:

$$N = \frac{AVm^{3/2}}{\sqrt{2\pi^2\hbar^3}} \times \frac{\sqrt{\pi k_B^3 T^3}}{2} \quad (\text{A1.36})$$

We can now eliminate  $A$  in Equation A1.32 by dividing through by Equation A1.36 for  $N$ , and hence calculating the *fraction* of the particles  $dN/N$  which occupy quantum states with energies in the range  $E$  to  $E + dE$ . We find :

$$\frac{dN}{N} = \frac{\frac{Vm^{3/2}}{\sqrt{2\pi^2\hbar^3}} E^{1/2} A \exp\left[\frac{-E}{k_B T}\right] dE}{\frac{AVm^{3/2}}{\sqrt{2\pi^2\hbar^3}} \times \frac{\sqrt{\pi k_B^3 T^3}}{2}} \quad (\text{A1.37})$$

$$\frac{dN}{N} = 2 \sqrt{\frac{E}{\pi k_B^3 T^3}} \exp\left[\frac{-E}{k_B T}\right] dE \quad (\text{A1.38})$$

We may alternatively write this as the probability  $P(E)dE$  that a molecule has energy between  $E$  and  $E + dE$ :

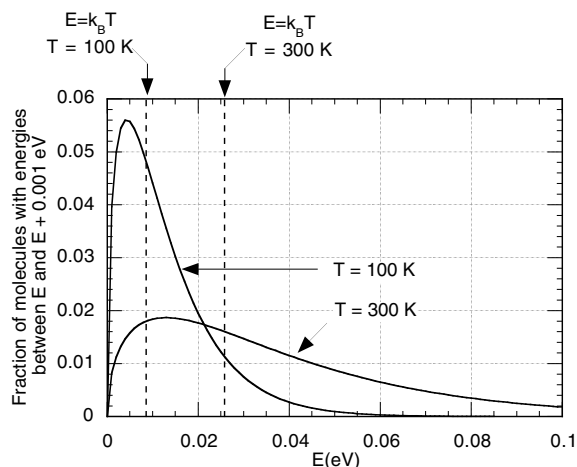
$$P(E)dE = 2 \sqrt{\frac{E}{\pi k_B^3 T^3}} \exp\left[\frac{-E}{k_B T}\right] dE \quad (\text{A1.39})$$

It is important to take note of the general form of Equation A1.39 which we may write more simply as:

$$P(E)dE = \text{constants} \times \sqrt{E} \times \exp\left[\frac{-E}{k_B T}\right] \quad (\text{A1.40})$$

We see that, at a given temperature, Equation A1.39 predicts *exactly the same* distribution of molecular energies for *all gases*. Example A1.1 shows how the curve may be used to make calculations about energy distribution in gases.

**Figure A1.5** The distribution of energies of molecules in a gas at temperatures of 100 K and 300 K. Notice that the curves are universal, i.e. they apply to all simple molecules whatever their mass. Heavy molecules move more slowly than lighter molecules in such a way as to keep the energies their same.



## A1.5 The distribution of molecular speeds

We are now close to completing the task we set ourselves: to calculate the distribution of molecular speeds. To achieve this, we need to convert the references to energy  $E$  in Equation A1.38:

$$\frac{dN}{N} = 2 \sqrt{\frac{E}{\pi k_B^3 T^3}} \exp\left[\frac{-E}{k_B T}\right] dE \quad (\text{A1.38}^*)$$

into references to molecular speed, using:

$$E = \frac{1}{2} m v^2 \quad (\text{A1.42})$$

and:

$$dE = m v dv \quad (\text{A1.43})$$

Notice that these substitutions assume the molecules have only the three degrees of freedom associated with molecular motion, and so we are implicitly neglecting the possibility of internal molecular vibrations and rotations. In fact, the presence or absence of these other degrees of freedom does not affect the conclusions that we draw here. On substituting Equations A1.42 and A1.43 into A1.38 we find:

$$\frac{dN}{N} = 2 \sqrt{\frac{\frac{1}{2} m v^2}{\pi k_B^3 T^3}} \exp\left[\frac{-m v^2}{2 k_B T}\right] m v dv \quad (\text{A1.44})$$

which simplifies to:

$$\frac{dN}{N} = \sqrt{\frac{2}{\pi}} \left[ \frac{m}{k_B T} \right]^{3/2} v^2 \exp\left[\frac{-m v^2}{2 k_B T}\right] dv \quad (\text{A1.45})$$

In terms of the probability that a molecule has a speed between  $v$  and  $v + dv$ ,  $P(v)dv$ :

$$P(v)dv = \sqrt{\frac{2}{\pi}} \left[ \frac{m}{k_B T} \right]^{3/2} v^2 \exp\left[\frac{-m v^2}{2 k_B T}\right] dv \quad (\text{A1.46})$$

This is the Maxwellian speed distribution curve. If you think its derivation from the ‘particle in a box’ problem has been magical, then consider this. Maxwell derived this curve 150 years ago, around 70 years before the discovery of quantum mechanics! The salient features of the curve are illustrated in Figures 4.6 to 4.8. An animation of the way in which the curve changes with temperature may be found on the web site for the book at [www.physicsofmatter.com](http://www.physicsofmatter.com)

Example A1.2 shows how the curve is used to make calculations about speed distributions in gases.

**Example A1.1**

In a gas at temperature  $T$ , what fraction of molecules have energies greater than  $k_B T$ , given that:

$$\int_{x=1}^{x=\infty} x^{1/2} e^{-x} dx = 0.507$$

The required fraction is the integral of  $dN/N$  (Equation A1.39) over the energy range specified, which in this case is from  $E = k_B T$  to infinity. So:

$$\text{fraction} = \int_{E=k_B T}^{E=\infty} 2 \sqrt{\frac{E}{\pi k_B^3 T^3}} e^{-E/k_B T} dE$$

If we substitute  $x = E/k_B T$  we find  $dx = dE/k_B T$  and the integral becomes:

$$\text{fraction} = \int_{x=1}^{x=\infty} \left[ 2 \sqrt{\frac{1}{\pi k_B^3 T^3}} \right] x^{1/2} e^{-x} k_B T dx$$

Taking the constants outside the integral sign, allows us to recognise the integral given in the question:

$$\text{fraction} = \left[ 2 \sqrt{\frac{1}{\pi}} \right] \int_{x=1}^{x=\infty} x^{1/2} e^{-x} dx$$

and substituting for this integral we have:

$$\text{fraction} = \left[ 2 \sqrt{\frac{1}{\pi}} \right] \times 0.507 = 0.572$$

Thus 57.2% of molecules have energy greater than  $k_B T$ . Notice that this is true at any temperature!

**Example A1.2**

In a nitrogen gas at 300 K, what fraction of molecules have speeds greater than  $10^3 \text{ ms}^{-1}$ , given that:

$$\int_{x=5.615}^{x=\infty} x^{1/2} e^{-x} dx = 9.345 \times 10^{-3}$$

The required fraction is the integral of  $P(v)dv$  (Equation A1.46) over the speed range specified, which in this case is from  $v = 10^3 \text{ ms}^{-1}$  to infinity. So:

$$\int_{v=10^6}^{v=\infty} P(v)dv = \int_{v=10^6}^{v=\infty} \sqrt{\frac{2}{\pi}} \left[ \frac{m}{k_B T} \right]^{3/2} v^2 e^{-mv^2/2k_B T} dv$$

If we substitute  $x = mv^2/2k_B T$  then  $dx = dv \sqrt{\frac{2m}{k_B T}}$  and the integral becomes:

$$\text{fraction} = \sqrt{\frac{2}{\pi}} \left[ \frac{m}{k_B T} \right]^{3/2} \int_{x=x_1}^{x=\infty} \frac{2k_B T x}{m} e^{-x} \frac{dx}{\sqrt{x}} \sqrt{\frac{k_B T}{2m}}$$

where the upper limit is infinity, and we will work out the  $x$ -value corresponding to the lower limit presently. Taking the constants outside the integral sign:

$$\text{fraction} = \sqrt{\frac{2}{\pi}} \left[ \frac{m}{k_B T} \right]^{3/2} \frac{2k_B T}{m} \sqrt{\frac{k_B T}{2m}} \int_{x=x_1}^{x=\infty} x^{1/2} e^{-x} dx$$

and re-arranging:

$$\text{fraction} = 2 \sqrt{\frac{1}{\pi}} \left[ \frac{m}{k_B T} \right]^{3/2} \left[ \frac{k_B T}{m} \right]^{3/2} \int_{x=10^6}^{x=\infty} x^{1/2} e^{-x} dx$$

then cancelling we find:

$$\text{fraction} = 2 \sqrt{\frac{1}{\pi}} \int_{x=x_1}^{x=\infty} x^{1/2} e^{-x} dx$$

Again we are able to recognise the numerical integral given in the question. We need to evaluate the lower limit of the integral using  $x = mv^2/2k_B T$  we have:

$$x_1 = \frac{28 \times 1.66 \times 10^{-27} \times (10^3)^2}{2 \times 1.38 \times 10^{-23} \times 300} = 5.615$$

$$\text{fraction} = \left[ 2 \sqrt{\frac{1}{\pi}} \right] \int_{x=5.6 \times 10^6}^{x=\infty} x^{1/2} e^{-x} dx$$

and substituting for this integral we have:

$$\text{fraction} = \left[ 2 \sqrt{\frac{1}{\pi}} \right] \times 9.345 \times 10^{-3} = 0.0105$$

Thus just over 1% of molecules have speeds greater than  $10^3 \text{ ms}^{-1}$ .



# Derivation of speed of sound formulae

## A2.1 Introduction

Derivations of formulae for the speed of sound are similar for all types of sound waves in solids, liquids and gases. Here we consider the derivation of formula first for the speed of longitudinal sound waves in gases and solids, and then for shear sound waves in solids. Finally we consider relationships among the elastic moduli in solids.

All analyses of sound waves involve both small quantities (e.g. strain in a solid), and infinitesimal changes in these small quantities. This can make the analyses confusing at first so you will need to take particular care in the following sections.

## A2.2 Longitudinal sound waves in a gas

The situation of planes of gas perpendicular to the direction of propagation ( $x$ -direction) of a plane sound wave is illustrated in Figure A2.1. Our analysis focuses on the changes in pressure and volume close to two planes (1 and 2) within the gas. In the absence of a sound wave, the equilibrium pressure is  $P_0$  and planes 1 and 2 are located at  $x$  and  $x + \Delta x$  respectively. In the presence of a sound wave, the pressure at  $x$  oscillates about  $P_0$  and at any particular time the pressure at  $x$  is no longer in general the same as the pressure at  $x + \Delta x$ .

$x + \Delta x$ . The position of planes 1 and 2 changes from:

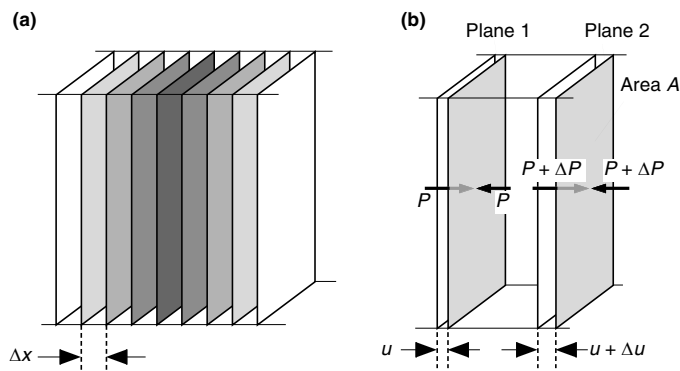
- $x$  and  $x + \Delta x$ , to
- $x + u$  and  $(x + \Delta x) + (u + \Delta u)$ .

Table A2.1 below is a systematic analysis of the shifts in position of these planes and of the resulting volume and pressure changes within the gas. The aim of the analysis is to deduce the net unbalanced force on the gas that originally lay between  $x$  and  $x + dx$ . We can then use Newton's Law  $F = ma$  to determine the dynamics of the gas, and hence deduce the speed of sound.

The effect of the sound wave is to compress (or rarefy) the gas which was originally between  $x$  and

It is important to notice the direction of the forces acting on the gas in Figure A2.1(b). The net force

**Figure A2.1** (a) A representation of the planes of constant pressure in a sound wave. The darkness of the shading indicates the amplitude of the pressure oscillations at a certain time. (b) Shows an analysis of the forces on a thin 'slab' of gas. It may help to refer to this figure when following the derivations in Table A2.1



**Table A2.1** Systematic derivation of the net force per unit area on the element of gas shown in Figure A2.1b.

	Value at $x$	Value at $x + dx$	Difference
<b>Displacement from equilibrium position</b>	$u$	$u + \Delta u$	$\Delta u$
<b>Fractional volume change</b> $\Delta V/V$	$\frac{A\Delta u}{A\Delta x} = \frac{\Delta u}{\Delta x} \approx \frac{\partial u}{\partial x}$	$\frac{A\Delta(u + \Delta u)}{A\Delta x} \approx \frac{\partial(u + \Delta u)}{\partial x}$ $= \frac{\partial u}{\partial x} + \frac{\partial}{\partial x}(\Delta u)$	$\left(\frac{\partial^2 u}{\partial x^2}\right)\Delta x$
Notice that if $\Delta u = 0$ then the gas is not compressed at all		Notice that we can also write $\Delta u$ as: $\Delta u = \left(\frac{\partial u}{\partial x}\right)\Delta x$ and so substitution yields: $= \frac{\partial u}{\partial x} + \frac{\partial}{\partial x}\left(\frac{\partial u}{\partial x}\right)\Delta x$ $= \frac{\partial u}{\partial x} + \left(\frac{\partial^2 u}{\partial x^2}\right)\Delta x$	
<b>Pressure change</b> $\Delta P = -\frac{1}{K} \frac{\Delta V}{V}$	$-\frac{1}{K} \frac{\partial u}{\partial x}$	$-\frac{1}{K} \frac{\partial u}{\partial x} - \frac{1}{K} \left(\frac{\partial^2 u}{\partial x^2}\right)\Delta x$	$-\frac{1}{K} \left(\frac{\partial^2 u}{\partial x^2}\right)\Delta x$
(by definition)			
<b>Force per unit area</b> $\Delta F = -\Delta P$ to the right in Figure A2.1(b)	$+\frac{1}{K} \frac{\partial u}{\partial x}$	$+\frac{1}{K} \frac{\partial u}{\partial x} + \frac{1}{K} \left(\frac{\partial^2 u}{\partial x^2}\right)\Delta x$	$+\frac{1}{K} \left(\frac{\partial^2 u}{\partial x^2}\right)\Delta x$

on the slab results from the sum of  $P$  acting to the right and  $P + \Delta P$  acting to the left. Notice that in the case indicated with  $\Delta u$  positive,  $\Delta P$  would be *negative* and the force on the gas would be in the positive  $x$  direction.

The mass of the gas originally between  $x$  and  $x + \Delta x$  is  $\Delta m = \rho A \Delta x$  where  $\rho$  is the density of the gas. The difference  $\Delta P$  between the pressure (force per unit area) at  $x$  and at  $x + \Delta x$  gives rise to acceleration of this mass. Note that the ‘background’ pressure corresponds to the ambient pressure within the gas and does not change with time. Recalling that we may write the acceleration of the gas as  $\partial^2 u / \partial t^2$  we write:

$$\Delta F = (\rho A \Delta x) \frac{\partial^2 u}{\partial t^2} \quad (\text{A2.1})$$

Dividing through by  $A$ , substituting for  $\Delta F/A = \Delta P$  from the rightmost column of Table A2.1 and cancelling yields:

$$\frac{1}{K} \frac{\partial^2 u}{\partial x^2} \Delta x = (\rho \Delta x) \frac{\partial^2 u}{\partial t^2} \quad (\text{A2.2})$$

$$\frac{\partial^2 u}{\partial x^2} = (K\rho) \frac{\partial^2 u}{\partial t^2} \quad (\text{A2.3})$$

Comparing Equation A2.3 with the standard form of the wave equation:

$$\left(\frac{\partial^2 f}{\partial x^2}\right) = \frac{1}{v^2} \left(\frac{\partial^2 f}{\partial t^2}\right) \quad (\text{A2.4})$$

where  $f(x)$  is the property that satisfies the wave equation. In this case we identify the displacement of the gas  $u$  as satisfying the wave equation with the speed of the displacement wave  $v$  given by:

$$v = \sqrt{\frac{1}{K\rho}} \quad (\text{A2.5})$$

Equation A2.5 is also commonly written in terms of the bulk modulus  $B$ :

$$v = \sqrt{\frac{B}{\rho}} \quad (\text{A2.6})$$

As outlined in §5.6.2, the bulk modulus and compressibility are those associated with *adiabatic* compression of the gas. Equation A2.6 also holds for liquids.

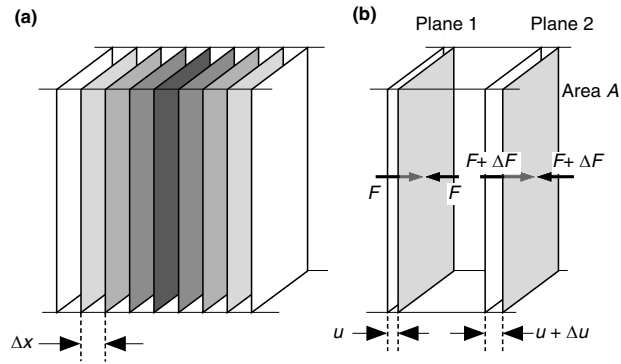
### A2.3 Longitudinal sound waves in solid rods

A longitudinal wave in a solid rod is illustrated in Figure A2.2 and the forces on an ‘elemental slab’ are analysed in Figure A2.2(b) and in Table A2.2. The derivations are similar to those for longitudinal waves in a gas described in §A1.1.

$\Delta m = \rho A \Delta x$  and the difference  $\Delta F$  between the tensile force per unit area at  $x$  and at  $x + \Delta x$  gives rise to acceleration of this mass. Note that the ‘background’ tensile force corresponds to a situation where  $\Delta u = 0$ , i.e. to a static background stress which does not change with time. Noticing that we may write the transverse acceleration of

The mass of the slab  $\Delta x$  per unit area is

**Figure A2.2** (a) A representation of the planes of constant pressure in a sound wave. The darkness of the shading indicates the amplitude of the pressure oscillations at a certain time. (b) Shows an analysis of the forces on a thin ‘slab’ of solid. It may help to refer to this figure when following the derivations in Table A2.2



**Table A2.2** Systematic derivation of the net tensile force per unit area on the element of solid shown in Figure A2.2b.

	Value at $x$	Value at $x + dx$	Difference
<b>Longitudinal displacement</b>	$u$	$u + \Delta u$	$\Delta u$
<b>Tensile strain</b>	$\varepsilon = \frac{\Delta u}{\Delta x} \approx \frac{\partial u}{\partial x}$	$\varepsilon + \Delta \varepsilon = \frac{\Delta(u + \Delta u)}{\Delta x}$ $\approx \frac{\partial(u + \Delta u)}{\partial x}$ $\approx \frac{\partial u}{\partial x} + \frac{\partial(\Delta u)}{\partial x}$	$\left( \frac{\partial^2 u}{\partial x^2} \right) \Delta x$
This is the <i>fractional</i> linear extension of the material originally between $x$ and $x + \Delta x$ .			
Notice that we can also write $\Delta u$ as:			
$\Delta u = \left( \frac{\partial u}{\partial x} \right) \Delta x$			
which substitutes to give:			
$\frac{\partial u}{\partial x} + \frac{\partial}{\partial x} \left( \frac{\partial u}{\partial x} \right) \Delta x$			
$\frac{\partial u}{\partial x} + \left( \frac{\partial^2 u}{\partial x^2} \right) \Delta x$			
<b>Tensile stress</b>	$S = E\varepsilon$ $= E \frac{\partial u}{\partial x}$	$S + \Delta S = E(\varepsilon + \Delta \varepsilon)$ $= E \frac{\partial u}{\partial x} + E \left( \frac{\partial^2 u}{\partial x^2} \right) \Delta x$	$E \left( \frac{\partial^2 u}{\partial x^2} \right) \Delta x$
<b>Tensile force per unit area</b>	$\frac{F}{A} = S = E\varepsilon = E \frac{\partial u}{\partial x}$	$\frac{F + \Delta F}{A} = E \frac{\partial u}{\partial x} + E \left( \frac{\partial^2 u}{\partial x^2} \right) \Delta x$	$\frac{\Delta F}{A} = E \left( \frac{\partial^2 u}{\partial x^2} \right) \Delta x$

the slab as  $\partial^2 u / \partial t^2$  we write:

$$\Delta F = (\rho A \Delta x) \frac{\partial^2 u}{\partial t^2} \quad (\text{A2.7})$$

Dividing through by  $A$ , substituting for  $dF/A$  from the rightmost column of Table A2.2, we find:

$$E \frac{\partial^2 u}{\partial x^2} \Delta x = (\rho \Delta x) \frac{\partial^2 u}{\partial t^2} \quad (\text{A2.8})$$

$$\frac{\partial^2 u}{\partial x^2} = \left( \frac{\rho}{E} \right) \frac{\partial^2 u}{\partial t^2} \quad (\text{A2.9})$$

Comparing Equation A2.9 with the standard form of the wave Equation (A2.4) shows that the speed of a longitudinal sound wave in a solid is:

$$v = \sqrt{\frac{E}{\rho}} \quad (\text{A2.10})$$

In fact, this formula is only appropriate to longitudinal sound waves along long thin rods. The formula for the speed of longitudinal sound waves in bulk solid is discussed in §A2.4 on *stresses in solids*

## A2.4 Transverse sound waves

A shear wave in a bulk solid is illustrated in Figure A2.3 and the forces on an elemental ‘slab’ are analysed in Figure A2.3(b) and in Table A2.3 below. The derivations are similar to those for longitudinal waves in a gas or a solid described previously.

The mass of the slab  $\Delta x$  is  $\Delta m = \rho A \Delta x$  and the difference  $\Delta F_s$  between the shear force per unit area at  $x$  and at  $x + \Delta x$  gives rise to acceleration of this mass. Note that the ‘background’ shear force  $F_s$  corresponds to a situation where  $\Delta u = 0$ , i.e. to static background shear which does not change with time. Recalling that we may write the transverse acceleration of the slab as  $\partial^2 u / \partial t^2$  we have:

$$\Delta F_s = (\rho A \Delta x) \frac{\partial^2 u}{\partial t^2} \quad (\text{A2.11})$$

Substituting for  $\Delta F_s/A$  and cancelling:

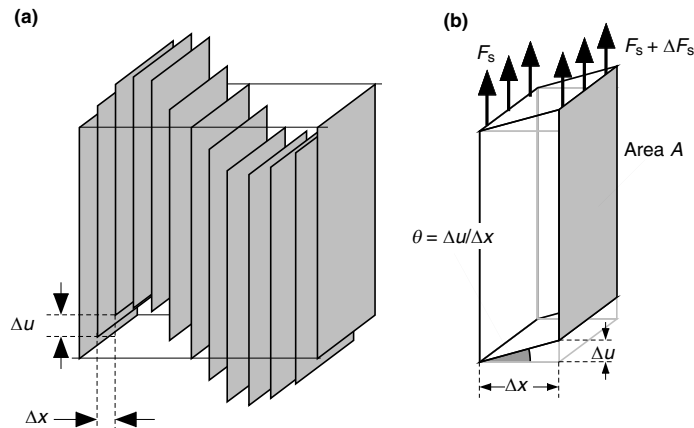
$$G \frac{\partial^2 u}{\partial x^2} \Delta x = (\rho \Delta x) \frac{\partial^2 u}{\partial t^2} \quad (\text{A2.12})$$

$$\frac{\partial^2 u}{\partial x^2} = \left( \frac{\rho}{G} \right) \frac{\partial^2 u}{\partial t^2} \quad (\text{A2.13})$$

Comparing Equation A2.13 with the standard form of the wave Equation (A2.4) shows that the speed of a shear wave in a solid is:

$$v_s = \sqrt{\frac{G}{\rho}} \quad (\text{A2.14})$$

**Figure A2.3** (a) A representation of the planes of constant shear in a sound wave. (b) Shows an analysis of the forces on a thin ‘slab’ of solid in a shear wave. It may help to refer to this figure when following the derivations in Table A2.3.



**Table A2.3** Systematic derivation of the net shear force per unit area on the element of solid shown in Figure A2.3b.

	Value at $x$	Value at $x + dx$	Difference
<b>Transverse displacement</b>	$u$	$u + \Delta u$	$\Delta u$
<b>Shear strain</b>	$\theta = \frac{\Delta u}{\Delta x}$ $\approx \frac{\partial u}{\partial x}$	$\theta + \Delta\theta = \frac{\Delta(u + \Delta u)}{\Delta x}$ $\approx \frac{\partial(u + \Delta u)}{\partial x}$ $= \frac{\partial u}{\partial x} + \frac{\partial}{\partial x}(\Delta u)$ We now write $\Delta u$ as: $\Delta u = \left(\frac{\partial u}{\partial x}\right)\Delta x$ which substitutes to give: $\theta + \Delta\theta = \frac{\partial u}{\partial x} + \frac{\partial^2 u}{\partial x^2}\Delta x$	$\Delta\theta = \left(\frac{\partial^2 u}{\partial x^2}\right)\Delta x$
<b>Shear stress</b>	$S_s = G\theta$ $= G \frac{\partial u}{\partial x}$	$S_s + \Delta S_s = G(\theta + \Delta\theta)$ $= G \frac{\partial u}{\partial x} + G \left(\frac{\partial^2 u}{\partial x^2}\right)\Delta x$	$\Delta S_s = G \left(\frac{\partial^2 u}{\partial x^2}\right)\Delta x$
<b>Shear force per unit area</b>	$\frac{F_s}{A} = S_s = G\theta = G \frac{\partial u}{\partial x}$	$\frac{F_s + \Delta F_s}{A} = G \frac{\partial u}{\partial x} + G \left(\frac{\partial^2 u}{\partial x^2}\right)\Delta x$	$\frac{\Delta F_s}{A} = G \left(\frac{\partial^2 u}{\partial x^2}\right)\Delta x$

## A2.5 Stresses in solids

Under tensile stresses, solids behave in a more complicated way than has been described hitherto. In the derivation of the speed of longitudinal sound waves in solids, we assumed that the only effect of a tensile (or compressive) stress was to extend (or shorten) the solid in the direction of the applied stress. However in reality a tensile (compressive) stress applied to a solid in the  $x$ -direction, causes the some compressive (tensile) stress in the  $y$ - and  $z$ - directions. Colloquially we say that the solid tends to ‘neck’ (‘bulge’).

In this section we consider the state of strain of a solid under applied tensile stress  $S_x$ ,  $S_y$ ,  $S_z$  in the  $x$ -,  $y$ - and  $z$ -directions respectively (Figure A2.4). Notice that the net stress in the  $x$ - direction is not just the directly applied stress  $S_x$  but  $+S_x - \sigma S_y - \sigma S_z$  where  $\sigma$  is the *Poisson ratio* (Example 7.8). Recall that  $\sigma$  describes the ratio of lateral to direct stress.

The minus signs arise because a tensile (+) stress in the  $y$ -direction results in a tendency to ‘neck’ in the  $x$ -direction i.e. in a compressive (–) strain. The net stress in the  $x$ -direction is related to the strain in the  $x$ -direction  $\Delta x/x$  by Young’s modulus  $E$ :

$$+S_x - \sigma S_y - \sigma S_z = E \frac{\Delta x}{x} \quad (\text{A2.15})$$

Assuming the elastic properties of the material are isotropic, similar equations hold for the net stresses in the  $y$ - and  $z$ -directions:

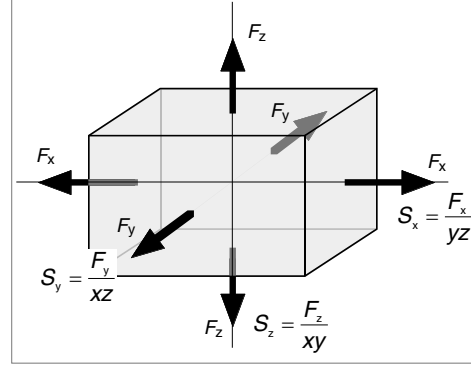
$$-\sigma S_x + S_y - \sigma S_z = E \frac{\Delta y}{y} \quad (\text{A2.16})$$

$$-\sigma S_x - \sigma S_y + S_z = E \frac{\Delta z}{z} \quad (\text{A2.17})$$

A longitudinal sound wave running along the

**Figure A2.4** A block of solid of dimensions  $x \times y \times z$  subjected to tensile stresses in each of the  $x$ -,  $y$ - and  $z$ -directions. The stress in the  $y$ - and  $z$ -directions also gives rise to stresses in the  $x$ -direction because of the rigidity of solids. The magnitude of the stress in the  $x$ -direction due to a stress in the  $y$ -direction defines the *Poisson ratio*  $\sigma$  according to:

$$\sigma = \frac{S_x}{S_y}$$



length of a long thin rod causes necking and bulging of the rod, but results in no unrelieved transverse stress, i.e. for a wave travelling in the  $x$ -direction,  $S_x$  and  $S_y$  are zero and Equation A2.15 becomes:

$$S_x = E \frac{\Delta x}{x} \quad (\text{A2.18})$$

This is the relationship we assumed in Table A2.2 between stress and strain, and so Equation A2.18 correctly applies to longitudinal sound waves on a long thin rod.

However, for a longitudinal sound wave in bulk solid, the presence of constraining material means the tendency to neck or bulge is resisted, and there are now unrelieved stresses transverse to the direction of motion of the wave. Thus for a wave travelling in the  $x$ -direction,  $S_y$  and  $S_z$  are generally not zero, however the lateral strains,  $\Delta y/y$  and  $\Delta z/z$  are constrained to be zero. In this case we rewrite Equations A2.15 to A2.17 as:

$$+S_x - \sigma S_y - \sigma S_z = +E \frac{\Delta x}{x} \quad (\text{A2.19})$$

$$-\sigma S_x + S_y - \sigma S_z = 0 \quad (\text{A2.20})$$

$$-\sigma S_x - \sigma S_y + S_z = 0 \quad (\text{A2.21})$$

If we solve the last two equations simultaneously, we find:

$$S_y = S_x \frac{\sigma}{(1-\sigma)} \quad \text{and} \quad S_z = S_x \frac{\sigma}{(1-\sigma)} \quad (\text{A2.22})$$

which may substituted in Equation A2.19 to yield:

$$+S_x - \sigma \left[ S_x \frac{\sigma}{(1-\sigma)} \right] - \sigma \left[ S_x \frac{\sigma}{(1-\sigma)} \right] = E \frac{\Delta x}{x} \quad (\text{A2.23})$$

Simplifying and rearranging yields:

$$S_x \left[ 1 - \frac{2\sigma^2}{(1-\sigma)} \right] = E \frac{\Delta x}{x} \quad (\text{A2.24})$$

$$S_x = \left[ \frac{1-\sigma-2\sigma^2}{(1-\sigma)} \right] E \frac{\Delta x}{x} \quad (\text{A2.25})$$

which may be written as:

$$S_x = \gamma E \frac{\Delta x}{x} \quad (\text{A2.26})$$

where  $\gamma$  is given by:

$$\gamma = \frac{(1+\sigma)(1-2\sigma)}{(1-\sigma)} \quad (\text{A2.27})$$

Comparing A2.26 with A2.18, we see that for a longitudinal wave in a bulk solid, we should have used an extra factor  $\gamma$  in the analysis of Table A2.2. We would then have found that the speed of longitudinal sound waves in a bulk solid would be:

$$v = \sqrt{\frac{\gamma E}{\rho}} \quad (\text{A2.28})$$

**Other useful expressions**

The situation shown in Figure A2.4 and summarised in the trio of equations A2.15 to A2.17, or A2.19 to A2.21 may also be used to link the bulk modulus  $B$  to Young's modulus  $E$ . If we consider the block in figure A2.3 to be under uniform tensile stress, the strain in all three directions will be equal, as will the stresses  $S_x$ ,  $S_y$ , and  $S_z$  be equal (to, say,  $S$ ). In this case the first of the trio of equations becomes:

$$S - \sigma S - \sigma S = E \frac{\Delta x}{x} \quad (\text{A2.29})$$

$$S(1 - 2\sigma) = E \frac{\Delta x}{x} \quad (\text{A2.30})$$

Notice that in this case of uniform stress  $S$  is just the force per unit area over the surface of the block. Furthermore, the fractional volume change  $\Delta V/V$  (Example 7.4) is given by  $3\Delta x/x$ . We can

thus rewrite Equation A2.30 as:

$$P = \left( \frac{E}{(1 - 2\sigma)} \right) \frac{\Delta x}{x} = \left( \frac{E}{3(1 - 2\sigma)} \right) \frac{\Delta V}{V} \quad (\text{A2.31})$$

Comparing this with the definition of the bulk modulus:

$$P = B \frac{\Delta V}{V} \quad (\text{A2.32})$$

we see that:

$$B = \frac{E}{3(1 - 2\sigma)} \quad (\text{A2.33})$$

Using similar techniques it may also be shown that:

$$G = \frac{E}{2(1 + \sigma)} \quad (\text{A2.34})$$





# The Gibbs free energy

## A3.1 The Gibbs free energy in equilibrium

Consider a sample of a substance  $A$  in contact with a reservoir maintained at temperature  $T$  and pressure  $P$ . Such a situation broadly represents the most common experimental situation for experiments on liquids and solids. Samples are held at a particular temperature, in a cryostat or furnace, and are free to adjust their volume. The pressure of their environment (commonly atmospheric pressure) remains constant, independent of any volume changes of the sample.

This situation is represented schematically in Figure A3.1. Notice that initially we do not assume that the sample is at temperature  $T$  and pressure  $P$ . We merely assume that it is in contact with reservoirs in such a situation.

Let us consider the entropy  $S_{\text{total}}$  of the combined system of the sample plus the reservoir, i.e. of  $A_{\text{Total}} = A + A'$ . Suppose there is a *spontaneous* exchange of heat between  $A$  and  $A'$ . Then since the total system is isolated, the entropy flow associated with such a heat flow must obey the second law of thermodynamics:

$$\Delta S_{\text{total}} = \Delta S + \Delta S' \geq 0 \quad (\text{A3.1})$$

Suppose that in this spontaneous process, some heat  $Q$  flows *from* the reservoir  $A'$  and is absorbed by the sample  $A$ . Then:

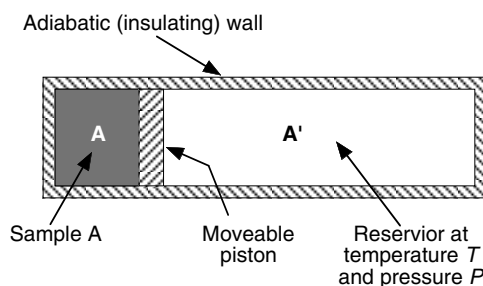
- Considering the definition of entropy and the heat flow *from*  $A'$  we conclude that the change in the entropy of the reservoir is:

$$\Delta S' = \frac{-Q}{T} \quad (\text{A3.2})$$

- Considering the first law of thermodynamics and the heat flow *into*  $A$  we conclude that:

$$Q = \Delta U + P\Delta V \quad (\text{A3.3})$$

**Figure A3.1** The conceptual framework for discussion of the circumstances at equilibrium of system  $A$  which is placed in contact with a reservoir at temperature  $T$  and pressure  $P$ . The processes which occur spontaneously are those which tend to minimise the sum of quantities known as the Gibbs free energy (Equation A3.10) and equilibrium is characterised by a minimum value of the Gibbs free energy.



Substituting A3.2 into A3.1 we have:

$$\Delta S_{\text{total}} = \Delta S - \frac{Q}{T} \quad (\text{A3.4})$$

Taking out a factor  $1/T$  this becomes:

$$\Delta S_{\text{total}} = \frac{1}{T} [T\Delta S - Q] \quad (\text{A3.5})$$

and substituting Equation A3.3 into A3.5 we find:

$$\Delta S_{\text{total}} = \frac{1}{T} [T\Delta S - (\Delta U + PV)] \quad (\text{A3.6})$$

This may be rewritten as:

$$\Delta S_{\text{total}} = \frac{1}{T} [\Delta(TS - U - PV)] \quad (\text{A3.7})$$

In A3.7 we have used the fact that when  $\Delta T$  and  $\Delta P$  are zero,  $\Delta(TS - U - PV)$  can be simplified. First we write the expression out in full and then simplify it as follows:

$$\begin{aligned}\Delta(TS - U - PV) &= T\Delta S + \underbrace{\Delta T}_{=0} - \Delta U - P\Delta V - \underbrace{V\Delta P}_{=0} \\ &= T\Delta S - \Delta U - P\Delta V\end{aligned}\quad (\text{A3.9})$$

This is only true when  $\Delta T$  and  $\Delta P$  are zero, i.e. when  $P$  and  $T$  are held constant. If we now define the Gibbs free energy  $G$  of the system  $A$  as:

$$G = U - TS + PV \quad (\text{A3.10})$$

then Equation A3.7 becomes:

$$\Delta S_{\text{total}} = \frac{-\Delta G}{T} \quad (\text{A3.11})$$

Thus the total entropy change  $\Delta S_{\text{total}}$  is now expressed in terms of quantities relating only to the system under study,  $A$ , and not to the reservoir. The second law of thermodynamics (Equation

A3.1) tells us that in spontaneous processes, the total entropy  $\Delta S_{\text{total}}$  can only either increase, or stay constant. Together with Equation A3.11 this implies:

$$\Delta G \leq 0. \quad (\text{A3.12})$$

In other words, if a sample  $A$  is placed in contact with a reservoir at temperature  $T$  and pressure  $P$ , the spontaneous processes which occur are such as to reduce the Gibbs free energy. So the equilibrium state is characterised by the Gibbs free energy attaining its minimum value.

You may also consult *Sears and Zemansky* (Published in 1996 by McGraw Hill College Division, ISBN: 0070170592) or *Reif* (Published in 1965 by McGraw-Hill Inc, ISBN: 007085615X) for further details.

# The Einstein and Debye theories of heat capacity

## A4.1 Introduction

Table A4.1 presents further details of the Einstein and Debye theories of the heat capacity of solids in such a way that their similarities become apparent. The main text has already stressed the key physical differences between the two theories (§7.6). The Einstein theory considers the thermal component of the internal energy  $U$  of a solid to be held by atoms vibrating *independently* in identical simple harmonic potentials. In contrast, the Debye theory considers the thermal component of the internal energy to be held by displacement (sound) waves.

- In the Einstein theory, the quantum states of the solid are the quantum states of each individual simple harmonic potential. All the quantum states have the same energy  $(n + \frac{1}{2})\hbar\omega_E$ . The thermal excitations of the solid are analogous to a set of fictitious particles which may multiply occupy a single quantum with energy  $E_E = \hbar\omega_E$ .
- In the Debye theory, the quantum states of the solid are considered to be wave-like states that are occupied by *phonons*. In order to work out the density of states one proceeds as in §6.5 or in Appendix A1. In §6.5 we showed that for electrons in a box the density of states varied like  $g(E) = A\sqrt{E}$  (Equation 6.70). We derived the density of states functions for molecules in box in Appendix A1 and found it

to have the same form (Equation A1.21). However, for phonons there are two key differences in the analysis. First, there is only one quantum state for each value of  $\mathbf{k} = (k_x, k_y, k_z)$ . Second, for phonons the energy is directly proportional to  $|\mathbf{k}|$  since the energy of a phonon is  $E = \hbar\omega = \hbar v|\mathbf{k}|$ . This expression has assumed that the speed of sound ( $v$ ) that relates the frequency to the wavelength is independent of wavelength. This is not quite correct for wavelengths of the order of a lattice spacing or so, but this is neglected in the Debye theory. The reader is referred to any advanced text on solid state physics for more details.

The Einstein theory predicts:

$$C = 3R \frac{\Theta_E^2 \exp(\Theta_E/T)}{T^2 [\exp(\Theta_E/T) - 1]^2} \quad (\text{A4.1})$$

This function may be directly calculated once  $\Theta_E$  is determined. The Debye theory predicts:

$$C = 9R \left[ \frac{T^3}{\Theta_D^3} \right]_{x=0}^{x=\Theta_D/T} \int \frac{x^4 \exp(x)}{[\exp(x) - 1]^2} dx \quad (\text{A4.2})$$

This function is tabulated in Table 7.11.

Table A4.1

	Debye theory	Einstein theory
<b>Density of quantum states</b> This function is such that $g(E)dE$ is the number of individual quantum states with energies between $E$ and $E + dE$ .	There is a maximum phonon energy $E_D$ . There are no quantum states with energies greater than $E_D$ , and below $E_D$ the density of states varies as: $g(E) = AE^2$ where $A$ can be shown to have a value per mole of: $A = \frac{9R}{k_B^3 \Theta_D^3}$ where $\Theta_D$ is the Debye temperature of the solid given theoretically by: $\Theta_D^3 = \frac{18N_A \pi^2 \hbar^3}{k_2^3 V_M \left[ \frac{2}{c_T^3} + \frac{1}{c_L^3} \right]}$ where $c_T$ and $c_L$ are the speeds of sound of transverse and longitudinal sound and $V_M$ is the volume of one mole of the solid.	All quantum states have the same energy $E_E$ and in 1 mole of elemental solid the density of states is: $g(E) = 3N_A \delta(E - E_E)$ where $\delta(E - E_E)$ is a delta function which is zero at all values of $E$ except $E_E$ where it is extremely large. Its integral over energy is defined to be 1.
<b>Occupation function</b> This function yields the average occupancy of an individual quantum state with energy $E$ when a system of particles in equilibrium at temperature $T$ .	The phonons are considered to be non-conserved bosons and so their occupation function is $f_{BE}$ (§2.5.3 Equation 2.62). The value of the chemical potential $\mu$ is zero because these bosons are not conserved (phonons may be destroyed and created). $f_{BE}(E, T) = \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1}$	The excitations of atoms of the solid are considered as non-conserved bosons and so their occupation function is $f_{BE}$ (§2.4.3 Equation 2.62). The value of the chemical potential $\mu$ is zero because these excitations may be destroyed or created. $f_{BE}(E, T) = \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1}$
<b>Distribution function</b> This function is such that the number of particles ( $dN$ ) occupying quantum states with energies between $E$ and $E + dE$ is $D(E)dE = f(E, T) g(E)dE$	By definition: $dN = D(E, T)dE = f_{BE}(E, T)g(E)dE$ so the number of phonons in one mole of solid at temperature $T$ is: $N = \int_0^{E_D} \frac{AE^2}{\exp\left(\frac{E}{k_B T}\right) - 1} dE$	By definition: $dN = D(E, T)dE = f_{BE}(E, T)g(E)dE$ so the number of excitations in the solid at temperature $T$ is: $N = \int_0^{\infty} \frac{3N_A \delta(E - E_E)}{\exp\left(\frac{E}{k_B T}\right) - 1} dE = \frac{3N_A}{\exp\left(\frac{E_E}{k_B T}\right) - 1}$
<b>Total internal energy</b> (Neglecting the cohesive energy $U_0$ )	$dU = ED(E, T) = Ef_{BE}(E, T)g(E)dE$ $U = \int_0^{E_D} f_{BE}(E, T)Eg(E)dE = \int_0^{E_D} \frac{AE^3}{\exp\left(\frac{E}{k_B T}\right) - 1} dE$	$dU = ED(E, T) = Ef_{BE}(E, T)g(E)dE$ $U = \int_0^{E_D} f_{BE}(E, T)Eg(E)dE = \frac{3E_E N_A}{\exp\left(\frac{E_E}{k_B T}\right) - 1}$

Debye theory	Einstein theory	
<p><b>Heat capacity</b></p> <p>Since neither of these theories consider the anharmonic interatomic potentials that give rise to thermal expansion, both these estimates for the heat capacity are estimates of <math>C_v</math> the molar heat capacity at constant volume.</p>	<p>By definition:</p> $C = \frac{dU}{dT}$ $= \frac{\partial}{\partial T} \left[ \int_0^{E_D} \frac{AE^3}{\exp\left(\frac{E}{k_B T}\right) - 1} dE \right]$ <p>Noticing that the integral is with respect to energy, we can take the differentiation inside the integral sign.</p> $C = \int_0^{E_D} AE^3 \frac{\partial}{\partial T} \left[ \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1} \right] dE$ $C = \int_0^{E_D} AE^3 \times \frac{-1 \times \left[ \frac{-E}{k_B T^2} \right]}{\left[ \exp\left(\frac{E}{k_B T}\right) - 1 \right]^2} \times \exp\left(\frac{E}{k_B T}\right) dE$ $C = \int_0^{E_D} \frac{AE^4 \exp\left(\frac{E}{k_B T}\right)}{\left[ \exp\left(\frac{E}{k_B T}\right) - 1 \right]^2} \times \frac{1}{k_B T^2} dE$ <p>We can solve this integral by substituting:</p> $x = \frac{E}{k_B T} \text{ i.e. } dE = k_B T dx$ $C = \int_0^{x_D} \left( \frac{A(k_B T)^4 x^4 e^x}{(e^x - 1)^2} \times \frac{1}{k_B T^2} \right) k_B T dx$ <p>Taking non <math>x</math>-dependent factors outside the integral we find:</p> $C = A k_B^4 T^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx$ <p>The value of integral must (in general) be evaluated numerically. Noticing that the upper limit for the integral may be written as <math>\theta_D/T</math> and substituting for <math>A</math> we find:</p> $C = 9R \left[ \frac{T^3}{\Theta^3} \right] \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$ <p style="text-align: center;"><b>Debye prediction</b></p>	<p>By definition:</p> $C = \frac{dU}{dT}$ $= \frac{\partial}{\partial T} \left[ \frac{3E_E N_A}{\exp\left(\frac{E_E}{k_B T}\right) - 1} \right]$ $C = \frac{-3E_E N_A}{\left[ \exp\left(\frac{E_E}{k_B T}\right) - 1 \right]^2} \times \frac{-E_E}{k_B T^2} \times \exp\left(\frac{E_E}{k_B T}\right)$ $C = \frac{3E_E^2 N_A}{k_B T^2 \left[ \exp\left(\frac{E_E}{k_B T}\right) - 1 \right]^2} \times \exp\left(\frac{E_E}{k_B T}\right)$ $C = 3R \times \frac{E_E^2}{k_B^2 T^2 \left[ \exp\left(\frac{E_E}{k_B T}\right) - 1 \right]^2} \times \exp\left(\frac{E_E}{k_B T}\right)$ <p>This may be written in terms of the Einstein temperature as:</p> $C = 3R \frac{\Theta_E^2}{T^2 \left[ \exp\left(\frac{\Theta_E}{T}\right) - 1 \right]^2} \times \exp\left(\frac{\Theta_E}{T}\right)$ <p style="text-align: center;"><b>Einstein prediction</b></p>



# Derivation of formula for bulk modulus

## A5.1 Bulk modulus of noble gas solids

In this appendix we show the mathematical steps required to derive the formulae for the bulk modulus of noble gas solids. This was a topic we covered in §7.3 on the compressibility of solids. The task at hand is to evaluate the formula for the bulk modulus  $B$ :

$$B = V \left. \frac{\partial^2 U}{\partial V^2} \right|_{V=V_0} \quad (7.4^* \text{ \& A5.1})$$

where  $U$  is the molar internal energy. The subscript indicates that we are to evaluate  $\partial^2 U / \partial V^2$  at the equilibrium volume:  $V = V_0$ . For molecular solids, we consider only the internal energy at  $T = 0$  K. In this case:

$$\begin{aligned} U &= -2\varepsilon N_A \left[ A_6 \left( \frac{\sigma}{r_0} \right)^6 - A_{12} \left( \frac{\sigma}{r_0} \right)^{12} \right] \\ &= 2\varepsilon N_A \left[ A_{12} \left( \frac{\sigma}{r_0} \right)^{12} - A_6 \left( \frac{\sigma}{r_0} \right)^6 \right] \end{aligned} \quad (6.18^*)$$

This expresses  $U$  as a function of  $r_0$ , the equilibrium separation between atoms. In order to evaluate A5.1 we need to find the relationship between the volume of the solid and  $r_0$ . We know from §6.2.5 that the equilibrium crystal structure is face-centred cubic, so we can write the molar volume as a function of  $r_0$ :

$$V = \frac{N_A}{4} (\sqrt{2} r_0)^3 = \frac{N_A}{\sqrt{2}} r_0^3 \quad (A5.2)$$

Differentiating we find:

$$\frac{\partial V}{\partial r_0} = 3 \frac{N_A}{\sqrt{2}} r_0^2 \quad (A5.3)$$

which we can rewrite as:

$$\frac{\partial r_0}{\partial V} = \frac{r_0}{3V} \quad (A5.4)$$

We can use this expression as follows. Proceeding in two steps, we change the variable of differentiation from  $V$  to  $r_0$ :

$$\begin{aligned} B &= V \frac{\partial^2 U}{\partial V^2} \\ &= V \left[ \frac{\partial r_0}{\partial V} \right]^2 \frac{\partial^2 U}{\partial r_0^2} \\ &= V \left[ \frac{r_0}{3V} \right]^2 \frac{\partial^2 U}{\partial r_0^2} \end{aligned} \quad (A5.5)$$

Now we substitute for  $U$  and differentiate twice:

$$\begin{aligned} B &= V \left[ \frac{r_0}{3V} \right]^2 \frac{\partial^2}{\partial r_0^2} \left( 2N_A \varepsilon \left[ A_{12} \left( \frac{\sigma}{r_0} \right)^{12} - A_6 \left( \frac{\sigma}{r_0} \right)^6 \right] \right) \\ &= V \left[ \frac{r_0}{3V} \right]^2 \frac{\partial}{\partial r_0} \left( 2N_A \varepsilon \left[ -\frac{12}{r_0} A_{12} \left( \frac{\sigma}{r_0} \right)^{12} + \frac{6}{r_0} A_6 \left( \frac{\sigma}{r_0} \right)^6 \right] \right) \\ &= V \left[ \frac{r_0^2}{9V^2} \right] \left( 2N_A \varepsilon \left[ \frac{12 \times 13}{r_0^2} A_{12} \left( \frac{\sigma}{r_0} \right)^{12} - \frac{6 \times 7}{r_0^2} A_6 \left( \frac{\sigma}{r_0} \right)^6 \right] \right) \end{aligned} \quad (A5.6)$$

Now we simplify this expression and collect terms to find:

$$\begin{aligned} B &= 2N_A \varepsilon \left[ \frac{1}{9V} \right] \left[ \left[ \frac{12 \times 13}{1} A_{12} \left( \frac{\sigma}{r_0} \right)^{12} - \frac{6 \times 7}{1} A_6 \left( \frac{\sigma}{r_0} \right)^6 \right] \right] \\ &= \left[ \frac{2N_A \varepsilon}{9V} \right] \left[ 156 A_{12} \left( \frac{\sigma}{r_0} \right)^{12} - 42 A_6 \left( \frac{\sigma}{r_0} \right)^6 \right] \end{aligned} \quad (A5.7)$$

We can now substitute the equilibrium value of  $\sigma/r_0$  as determined by Equation 6.22

$$\left[\frac{\sigma}{r_0}\right]^6 = \left[\frac{A_6}{2A_{12}}\right] \quad (*6.23)$$

And substitute this into Equation A5.7:

$$B = \frac{2N_A \varepsilon}{9V} \left[ 156A_{12} \left[ \frac{A_6}{2A_{12}} \right]^2 - 42A_6 \left[ \frac{A_6}{2A_{12}} \right] \right] \quad (A5.8)$$

We simplify the expression for  $B$  in several stages:

$$\begin{aligned} B &= \frac{2N_A \varepsilon}{9V} \left[ \frac{156}{4} - \frac{42}{2} \right] \left[ \frac{A_6^2}{A_{12}} \right] \\ &= \frac{2N_A \varepsilon}{9V} [39 - 21] \left[ \frac{A_6^2}{A_{12}} \right] \\ &= \frac{2N_A \varepsilon}{9V} [18] \left[ \frac{A_6^2}{A_{12}} \right] \\ &= \frac{4N_A \varepsilon}{V} \left[ \frac{A_6^2}{A_{12}} \right] \end{aligned} \quad (A5.9)$$

Now we substitute for  $V$  in this expression using A5.2, which itself needs to be evaluated at the equilibrium separation A5.2. So we evaluate the molar volume as:

$$\begin{aligned} V &= \frac{N_A}{\sqrt{2}} r_0^3 \\ &= \frac{N_A}{\sqrt{2}} \sigma^3 \left[ \frac{2A_{12}}{A_6} \right]^{1/2} \end{aligned} \quad (A5.10)$$

We can substitute for  $V$  (Equation A5.10) into Equation A5.9:

$$B = \frac{4N_A \varepsilon}{\underbrace{\left[ \frac{N_A}{\sqrt{2}} \sigma^3 \left[ \frac{2A_{12}}{A_6} \right]^{1/2} \right]}_V} \left[ \frac{A_6^2}{A_{12}} \right] \quad (A5.11)$$

and simplify this by cancelling terms:

$$\begin{aligned} B &= \frac{4N_A \varepsilon}{\frac{N_A}{\sqrt{2}} \sigma^3 \left[ \frac{2A_{12}}{A_6} \right]^{1/2}} \left[ \frac{A_6^2}{A_{12}} \right] \\ &= \frac{4\varepsilon}{\sigma^3} \left[ \frac{A_6^{5/2}}{A_{12}^{3/2}} \right] \end{aligned} \quad (A5.12)$$

Now we substitute  $A_{12} = 12.13$  and  $A_6 = 14.45$  for the *fcc* structure (Table 6.1) to find:

$$B = 75.12 \frac{\varepsilon}{\sigma^3} \quad (A5.13)$$

To evaluate this for a particular substance we use values from Table 6.2 for the range parameter  $\sigma$  and the energy parameter  $\varepsilon$ . For example for argon we find:

$$\begin{aligned} B &= 75.12 \frac{\varepsilon}{\sigma^3} \\ &= 75.12 \times \frac{10.3 \times 1.6 \times 10^{-22}}{(0.344 \times 10^{-9})^3} \\ &= 75.12 \times 4.05 \times 10^7 \\ &= 3.041 \times 10^9 \text{ Pa} \\ &= 3.041 \text{ GPa} \end{aligned} \quad (A5.14)$$

This may be compared with the experimental value of  $2.7 \times 10^9$  Pa (2.7 GPa). The calculated values for the other noble gas solids are tabulated in Table 7.6.