12.1 Introduction and synopsis

Heat, until about 1800, was thought to be a physical substance called 'caloric' that somehow seeped into things when they were exposed to a flame. It took the American Benjamin Thompson[1], backed up by none other than the formidable Carnot[2], to suggest what we now know to be true – heat is atoms or molecules in motion. In gases, they fly between occasional collisions with each other. Solids, by contrast, vibrate about their mean positions, interacting with all their neighbours; the higher the temperature, the greater the amplitude of vibrations. From this perception emerges all of our understanding of the thermal properties of solids: their heat capacity, expansion coefficient, thermal conductivity, and even melting point.

Heat affects mechanical and physical properties too. As temperature rises, the elastic modulus decreases, the strength falls, and the material starts to creep, deforming slowly with time at a rate that increases as the melting point is approached until, on melting, the solid loses all stiffness and strength. This we leave for Chapter 13.

Thermal properties quantify the response of materials to heat. We use these properties in many ways. The chapter opening page shows an example, a copper heat exchanger, designed to transfer heat efficiently between two circulating fluids. This chapter describes thermal properties, their origins, the ways they can be manipulated, and the ways they are used in design and in manufacturing processes.

12.2 Thermal properties: definition and measurement

Reference temperatures Two temperatures, the *melting temperature*, T_m, and the *glass transition temperature*, T_g (units for both: Kelvin[3], K, or centigrade, °C), are fundamental points of reference because they relate directly to the strength of the bonds in the solid. Pure crystalline solids have a sharp melting point, T_m, abruptly changing state from solid to low-viscosity liquid. Alloys usually melt over a temperature range – but the onset and completion of melting are still at precise temperatures. Non-crystalline molecular materials such as thermoplastics have a more gradual transition from true solid to very viscous liquid, with the change being characterised by the glass transition temperature, T_g. It is helpful in engineering design to define two further reference temperatures: the *maximum* and *minimum service temperatures*, $T_{\max}$ and $T_{\min}$ (units for both: K or °C), established empirically from practical experience. The first tells us the highest temperature at which the material can be used continuously without oxidation, chemical change, or excessive

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[1] Benjamin Thompson (1753–1814), later Count Rumford, while in charge of the boring of cannons at the Watertown Arsenal near Boston, Massachusetts, noted how hot they became and formulated the 'mechanical equivalent of heat' – what we now call heat capacity.

[2] Nicolas Léonard Sadi Carnot (1796–1832), physicist and engineer as well as formulator of the Carnot cycle and the concept of entropy, the basis of the optimisation of heat engines. He died of cholera, a fate most physicists today, mercifully, are spared.

[3] William Thompson, Lord Kelvin (1824–1907), Scottish mathematician who contributed to many branches of physics; he was known for his self-confidence, which led him to claim (in 1900) that there was nothing more to be discovered in physics – he already knew it all.

distortion becoming a problem. The second is the temperature below which the material becomes brittle or otherwise unsafe to use.

Specific heat capacity It costs energy to heat a material up. The heat capacity or specific heat is the energy to heat 1 kg of a material by 1K, and since the measurement is usually made at constant pressure (atmospheric pressure) it is given the symbol C_p. Heat is measured in joules[4], symbol J, so the units of specific heat are J/kg.K. When dealing with gases, it is more usual to measure the heat capacity at constant volume (symbol C_v), and for gases this differs from C_p. For solids the difference is so slight that it can be ignored, and we shall do so here. C_p is measured by calorimetry, which is also the standard way of measuring the glass temperature, T_g. Figure 12.1 shows how, in principle, this is done. A measured quantity of energy (here, electrical energy) is pumped into a sample of material of known mass. The temperature rise is measured, allowing energy/kg.K to be calculated. Real calorimeters are more elaborate than this, but the principle is the same.

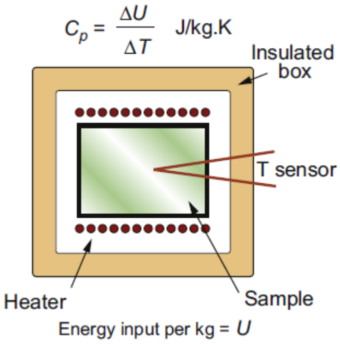

Figure 12.1 Measuring heat capacity, C_p.

Thermal expansion coefficient Most materials expand when they are heated (Figure 12.2). The thermal strain per degree of temperature change is measured by the linear thermal expansion coefficient, α. It is defined by

$$\alpha = \frac{1}{L}\frac{dL}{dT} \tag{12.1}$$

where L is a linear dimension of the body. If the material is anisotropic it expands differently in different directions, and two or more coefficients are required. Since strain is dimensionless, the units of α are K^{-1}, or more conveniently 'microstrain/K'; that is, $10^{-6}\,K^{-1}$. In some circumstances, we use the *volumetric* thermal expansion coefficient, α_v (the volumetric strain per Kelvin).

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[4] James Joule (1818–1889), English physicist, who, motivated by theological belief, sought to establish the unity of the forces of nature. His demonstration of the equivalence of heat and mechanical work did much to discredit the caloric theory.

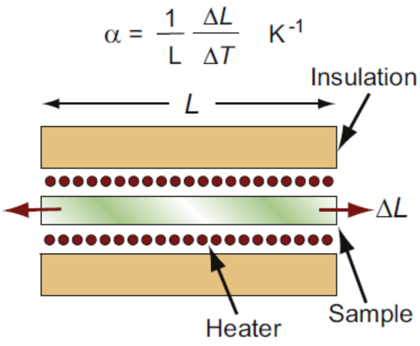

Figure 12.2 Measuring the thermal expansion coefficient, α.

Thermal conductivity and diffusivity The rate at which heat is conducted through a solid at steady-state (meaning that the temperature profile does not change with time) is measured by the *thermal conductivity*, λ (units: W/m.K). Figure 12.3 shows how it is measured: by recording the heat flux flowing through the material from a surface at higher temperature T_1 to a lower one at T_2 separated by a distance x. The conductivity is calculated from Fourier's[5] law:

$$q = -\lambda \frac{dT}{dx} = \lambda \frac{(T_1 - T_2)}{x} \tag{12.2}$$

where q is the heat flux per unit area, or power density. Power is measured in Watts[6] (Joules per second), so the units of power density are W/m^2.

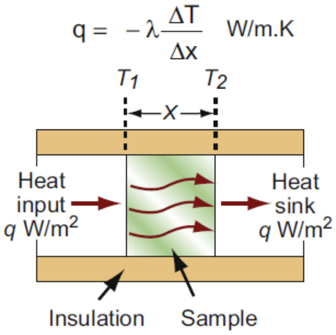

Figure 12.3 Measuring thermal conductivity, λ.

Thermal conductivity, as we have said, governs the flow of heat through a material at steady-state. The property governing transient heat flow (when temperature varies with time) is the *thermal diffusivity*, a (units: m^2/s). The two are related by

$$a = \frac{\lambda}{\rho C_p} \tag{12.3}$$

where ρ is the density and C_p is, as before, the heat capacity. The thermal diffusivity can be measured directly by measuring the time it takes for a temperature pulse to traverse a specimen of known thickness when a heat source is applied briefly to one side, or it can be calculated from λ (and ρC_p) via equation (12.3). Solutions to problems of transient heat flow, discussed later, have a time constant

$$t \approx \frac{x^2}{a}$$

where x is the distance that heat has penetrated in time t.

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[5] Baron Jean Baptiste Joseph Fourier (1768–1830), mathematician and physicist; he nearly came to grief during the French Revolution but survived to become one of the savants who accompanied Napoleon Bonaparte in his conquest of Egypt.

[6] James Watt (1736–1819), instrument maker and inventor of the condenser steam engine (the idea came to him while 'walking on a fine Sabbath afternoon'), which he doggedly developed. Unlike so many of the characters footnoted in this book, Watt, in his final years, was healthy, happy, and famous.

12.3 The big picture: thermal property charts

All materials have a thermal expansion coefficient α, a specific heat C_p, and a thermal conductivity λ (and hence a thermal diffusivity, a). Three charts give an overview of these thermal properties and their relationship to strength. The charts are particularly helpful in choosing materials for applications that use these properties or where failure may be a consequence of poor thermal design. Certain thermal behaviours, however, are shown by only a few special materials; shape-memory is an example. There is no point in making charts for these because so few materials have them, but they are still of engineering interest. Examples that use them are described near the end of Section 12.6.

Thermal expansion, α, and thermal conductivity, λ (Figure 12.4) Metals and technical ceramics have high conductivities and modest expansion coefficients; they lie towards the lower right of the chart. Polymers and elastomers have conductivities 100 times less and expansion coefficients 10 times greater than those of metals; they lie at the upper left. The chart shows contours of λ/α, a quantity important in designing against thermal distortion — a subject we return to in Section 12.6. An extra material, Invar (a nickel alloy), has been added to the chart because of its uniquely low expansion coefficient at and near room temperature, a consequence of a trade-off between normal expansion and contraction associated with a magnetic transformation.

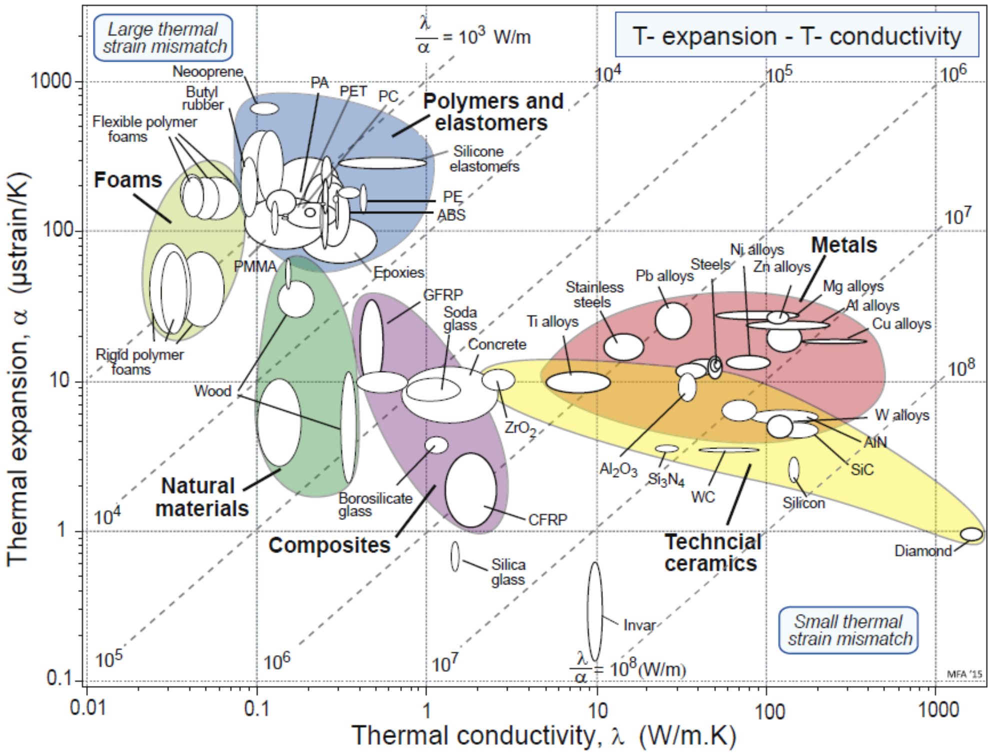

Figure 12.4 The linear thermal expansion coefficient, α, plotted against the thermal conductivity, λ. The contours show the thermal distortion parameter, λ/α.

Thermal conductivity, λ, and thermal diffusivity, a (Figure 12.5) Good conductors lie at the upper right, good insulators at the lower left. The data span almost 5 decades for λ and *a*. The diagonal contours show the ratio λ/*a*, equal to the volumetric heat capacity ρC_p. Solid materials are strung out along the line

$$\rho C_p \approx 3 \times 10^6 \ \mathrm{J/m^3.K} \tag{12.4}$$

meaning that the heat capacity per unit volume, ρC_p, is almost constant for all solids, something to remember for later. As a general rule, then,

$$\lambda \approx 3 \times 10^6 \ a \tag{12.5}$$

(λ in W/m.K and *a* in $\mathrm{m^2/s}$). Some materials deviate from this rule and have lower-than-average volumetric heat capacity. The largest deviations are shown by porous solids: foams, low-density firebrick, woods, and the like. Because of their low density, they contain fewer atoms per unit volume, and averaged over the volume of the structure, ρC_p is low. The result is that although foams have low *conductivities* (and are widely used for insulation because of this), their *thermal diffusivities* are not necessarily low. This means that they don't transmit much heat, but they do change temperature relatively quickly.

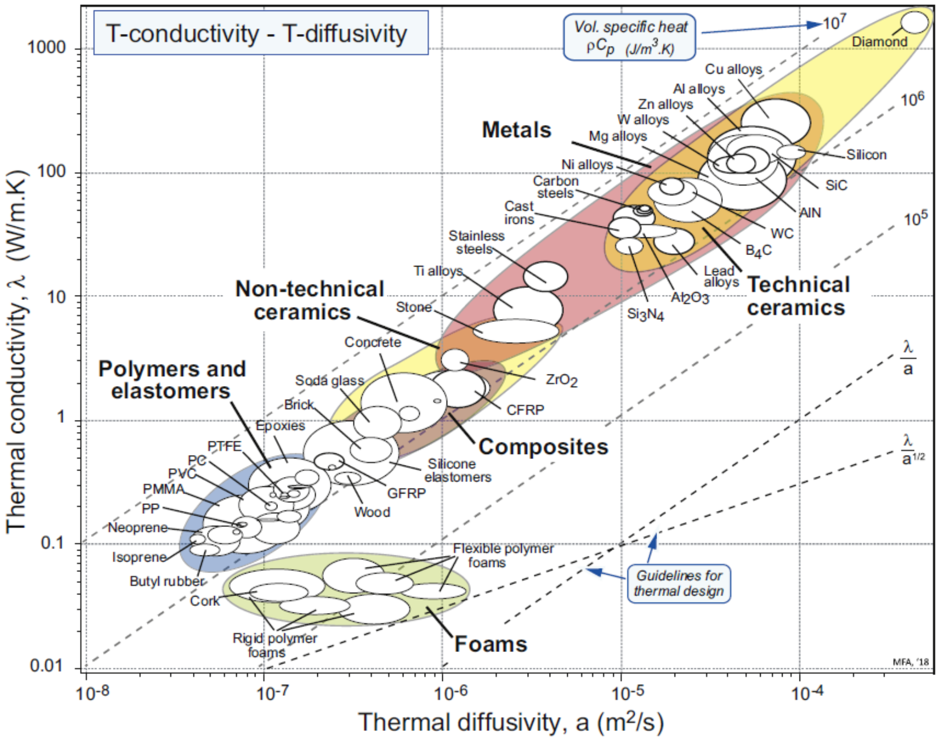

Figure 12.5 The thermal conductivity, λ, plotted against the thermal diffusivity, $a = \lambda/\rho C_p$. The contours show the specific heat per unit volume, ρC_p.

Thermal conductivity λ and yield strength σ_y (Figure 12.6) Metals, particularly the alloys of copper, aluminium, and nickel, are both strong and good conductors, a combination of properties we seek for applications such as heat exchangers, and one we return to in Section 12.6.

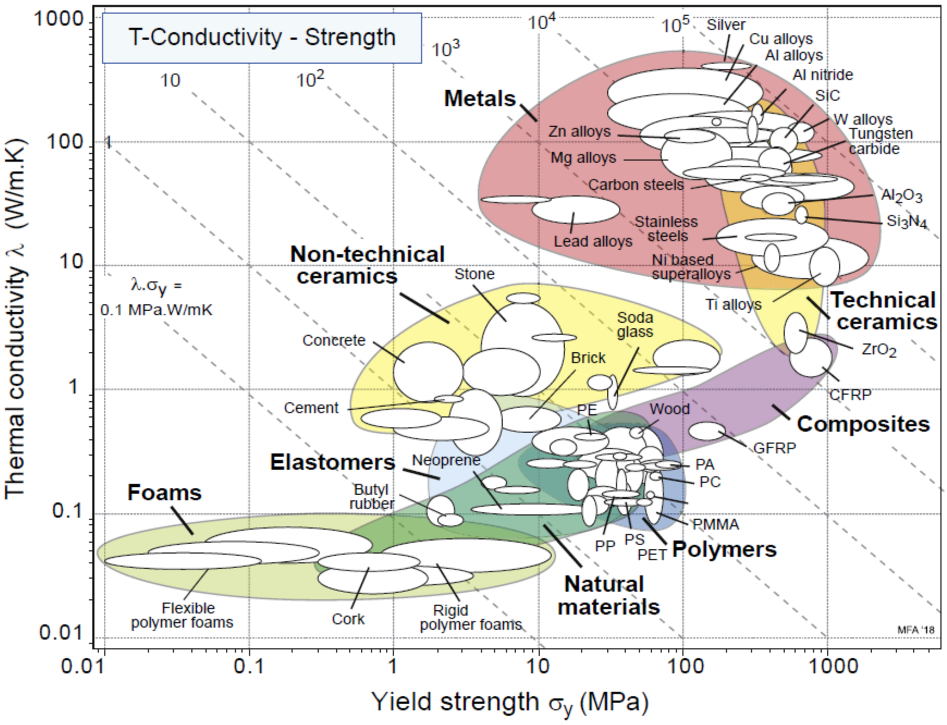

Figure 12.6 Thermal conductivity, λ, and strength, σ_y. The contours show the product $\lambda\sigma_y$.

12.4 Drilling down: the physics of thermal properties

Heat capacity We owe our understanding of heat capacity to Albert Einstein[7] and Peter Debye[8]. Heat, as already mentioned, is atoms in motion. Atoms in solids vibrate about their mean positions with an amplitude that increases with temperature, but they can't vibrate independently because they are coupled by their inter-atomic bonds; the vibrations are like standing elastic waves. Figure 12.7 shows that along any row of atoms, there is the possibility of one longitudinal mode and two transverse modes, one in the plane of the page and one normal to it. Some of these have short wavelengths and high energy, others long wavelengths and lower energy (Figure 12.8). The shortest possible wavelength, λ_1, is just twice the atomic spacing; the others are longer. A solid with N atoms has N discrete wavelengths, each with a longitudinal mode and two transverse modes, or $3N$ modes in all. Their amplitudes are such that on average, each has energy $k_B T$, where k_B is Boltzmann's constant[9], 1.38×10^{-23} J/K. If the volume occupied by an atom is Ω, then the number of atoms per unit volume is $N = 1/\Omega$ and the total thermal energy per unit volume in the material is $3k_\mathrm{B}T/\Omega$. The heat capacity per unit volume, ρC_p, is the *change* in this energy per Kelvin change in temperature, giving

$$\rho C_p = \frac{3k_B}{\Omega}\ \mathrm{J/m^3K} \tag{12.6}$$

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[7] Albert Einstein (1879–1955), patent officer, physicist, and campaigner for peace, one of the greatest scientific minds of the 20th century; he was forced to leave Germany in 1933, moving to Princeton, New Jersey, where his influence on US defence policy was profound.

[8] Peter Debye (1884–1966), Dutch physicist and Nobel Prize winner, did much of his early work in Germany until 1938, after being harassed by the Nazis, he moved to Cornell, New York, where he remained until his death.

[9] Ludwig Boltzmann (1844–1906), born and worked in Vienna at a time when that city was the intellectual centre of Europe; his childhood interest in butterflies evolved into a wider interest in science, culminating in his seminal contributions to statistical mechanics.

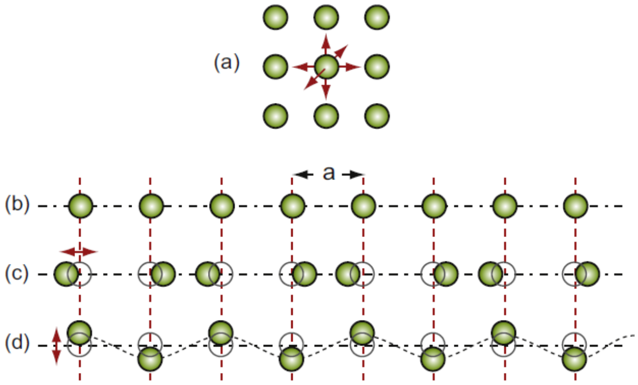

Figure 12.7 (a) An atom vibrating in the 'cage' of surrounding atoms, with 3 degrees of freedom, (b) a row of atoms at rest, (c) a longitudinal wave, and (d) one of two transverse waves (in the other, the atoms oscillate normal to the page).

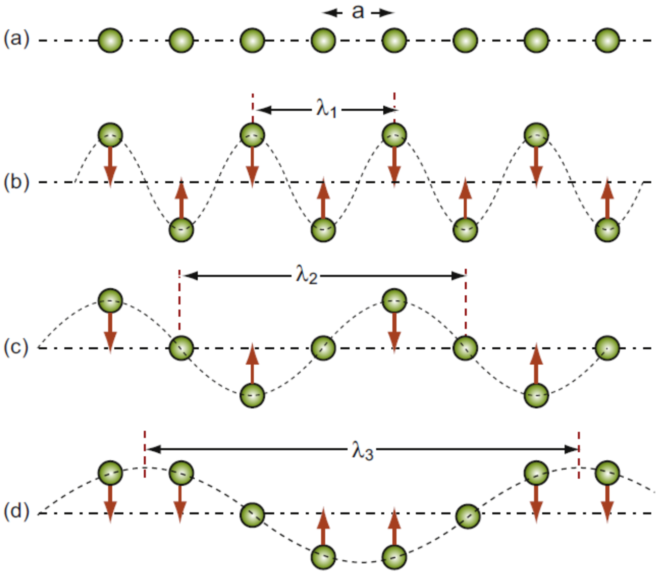

Figure 12.8 Thermal energy involves atomic vibrations. There is one longitudinal mode of vibration and two transverse modes, one of which is shown here. The shortest meaningful wavelength, $\lambda_1 = 2a$, is shown in (b).

Atomic volumes do not vary much; all lie within a factor of 3 of the value $2 \times 10^{-29}/\text{m}^3$, giving a volumetric heat capacity

$$\rho C_p \approx 2 \times 10^6 \ \text{J/m}^3\text{K} \tag{12.7}$$

The chart of Figure 12.5 shows that this is indeed the case.

Thermal expansion If a solid expands when heated (and almost all do), it must be because the atoms are moving farther apart. Figure 12.9 shows how this happens. It looks very like an earlier one, Figure 4.41, but there is a subtle difference: the force–spacing curve, a straight line in the earlier figure, is not in fact quite straight; the bonds become stiffer when the atoms are pushed together and less stiff when they are pulled apart. Atoms vibrating in the way described earlier oscillate about a mean spacing that increases with the amplitude of oscillation and thus with increasing temperatures. So thermal expansion is a non-linear effect; if the bonds between atoms were linear springs, there would be no expansion.

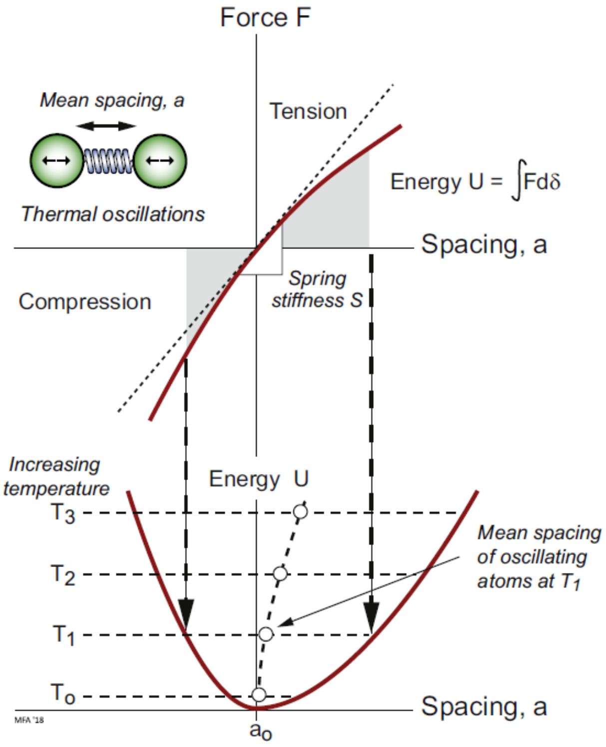

Figure 12.9 Thermal expansion results from the oscillation of atoms in an unsymmetrical energy well.

The stiffer the springs, the steeper the force–displacement curve and the narrower the energy well in which the atom sits, giving less scope for expansion. Thus materials with high modulus (stiff springs) have low expansion coefficients, whereas those with low modulus (soft springs) have high expansion – indeed, to a good approximation

$$\alpha \approx \frac{1.6 \times 10^{-3}}{E} \tag{12.8}$$

(E in GPa, α in K^{-1}). It is an empirical fact that all crystalline solids expand by about the same amount on heating from absolute zero to their melting point – about 2%. The expansion coefficient is the expansion per degree Kelvin, meaning that

$$\alpha \approx \frac{0.02}{T_m} \tag{12.9}$$

Tungsten, with a melting point of around 3330°C (3600 K), has $\alpha = 5 \times 10^{-6}$/K, whereas lead, with a melting point of about 330°C (600 K, six times lower than that of tungsten) expands six times more ($\alpha = 30 \times 10^{-6}$/K). Equation (12.9) (with T_m in Kelvin, of course) is a remarkably good approximation for the expansion coefficient.

Thermal conductivity Heat is transmitted through solids in three ways: by thermal vibrations; by the movement of free electrons in metals; and if they are transparent to infra-red, by radiation. Transmission by thermal vibrations involves the propagation of *elastic waves*. When a solid is heated, the heat enters as elastic wave packets or *phonons*. The phonons travel through the material, and like any elastic wave, they move with the speed of sound, c_o ($c_o \approx \sqrt{E/\rho}$). If this is so, why does heat not diffuse at the same speed? It is because phonons travel only a short distance before they are scattered by the slightest irregularity in the lattice of atoms through which they move, even by other phonons. On average they travel a distance called the *mean free path*, ℓ_m, before bouncing off something, and this path is short – typically less than 0.01 μm (10^{-8} m).

We calculate the conductivity by using a *net flux model*, much as you would calculate the rate at which cars accumulate in a car park by counting the rate at which they enter and subtracting the rate at which they leave. Phonon conduction can be understood in a similar way, as suggested by Figure 12.10. Here a rod with unit cross-section carries a uniform temperature gradient dT/dx between its ends. Phonons within it have 3 degrees of freedom of motion (they can travel in the $\pm x$, $\pm y$, and $\pm z$ directions). Focus on the mid-plane M–M. On average, one-sixth of the phonons are moving in the $+x$ direction; those within a distance ℓ_m of the plane will cross it from left to right before they are scattered, carrying with them an energy $\rho C_p(T + \Delta T)$ where T is the temperature at the plane M–M and $\Delta T = (dT/dx)\ell_m$. Another one-sixth of the phonons move in the $-x$ direction and cross M–M from right to left, carrying an energy $\rho C_p(T - \Delta T)$. Thus the energy flux q (J/m^2.s) across unit area of M–M per second is

$$\begin{aligned} q &= -\frac{1}{6}\rho C_p\, c_o \left(T + \frac{dT}{dx}\,\ell_m\right) + \frac{1}{6}\,\rho\, C_p\, c_o \left(T - \frac{dT}{dx}\,\ell_m\right) \\ &= -\frac{1}{3}\rho C_p\, \ell_m\, c_o \frac{dT}{dx} \end{aligned}$$

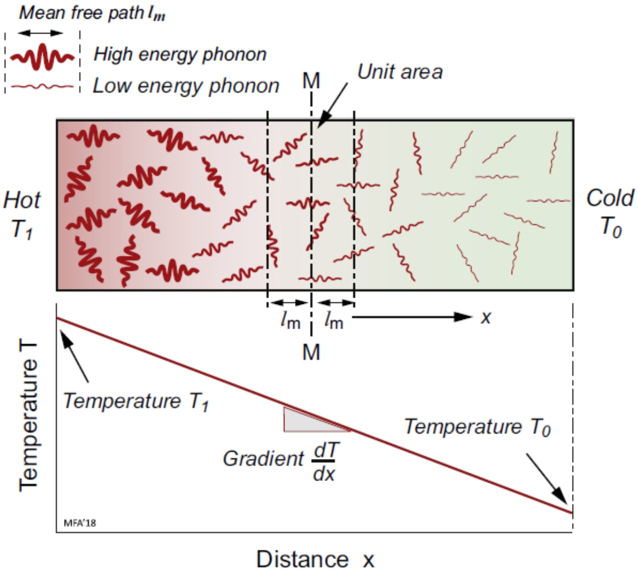

Figure 12.10 Transmission of heat by the motion of phonons.

Comparing this with the definition of thermal conductivity (equation (12.2)), we find the conductivity to be

$$\lambda = \frac{1}{3}\rho C_p \ell_m c_o \tag{12.10}$$

Sound waves are elastic waves, like phonons, but travel through the same bar without much scattering. Why do phonons scatter so readily? It's because waves are scattered most by obstacles with a size comparable to their wavelengths – that is how diffraction gratings work. Audible sound waves have wavelengths measured in metres, not microns; they are scattered by buildings (which is why you can't always tell where a police siren is coming from) but not by the atom-scale obstacles that scatter phonons, with wavelengths starting at two atomic spacings (Figure 12.8).

Phonons contribute little to the conductivity of pure metals such as copper or aluminium because the heat is carried more rapidly by the free electrons. Equation (12.10) still applies, but now C_p, c_o, and ℓ_m become the specific heat capacity, and the velocity and the mean free path of the electrons. Free electrons also conduct electricity, with the result that metals with high electrical conductivity also have high thermal conductivity (the Wiedemann–Franz law), as will be illustrated in Chapter 15.

12.5 Manipulating thermal properties

Thermal expansion Expansion can be a problem, generating thermal stress and causing distortion, which is bad in conventional structures and catastrophic in precise mechanisms and instruments. The expansion coefficient α, like modulus or melting point, depends on the stiffness and strength of atomic bonds. There's not much that can be done about these, so the expansion coefficient of a material is normally beyond our control. A few materials have exceptionally low expansion – borosilicate glass (Pyrex), silica, and carbon fibres, for example – but they are hard to use in engineering structures. There is one exception – the family of alloys called *Invars*. They achieve very low expansion by the trick of cancelling the thermal expansion (which is in fact happening) with a contraction caused by the gradual loss of magnetism as the material is heated.

Thermal conductivity and heat capacity Equation (12.10) describes thermal conductivity. Which of the terms it contains can be manipulated and which cannot? The volumetric heat capacity ρC_p, as we have seen, is almost the same for all solid materials. The sound velocity $c_o \approx \sqrt{E/\rho}$ depends on two properties that are not easily changed (in fully dense solids). That leaves the mean free path, ℓ_m, of the phonons, or in metals, of the electrons. Introducing *scattering centres* such as impurity atoms or finely dispersed particles reduces ℓ_m; taking them out (by increasing purity) increases it. Thus the conductivity of pure iron is 80 W/m.K, while that of stainless steel – iron with up to 30% of nickel and chromium in solution – is only 18 W/m.K. Certain materials can exist in a glassy state, and here the disordered nature of the glass makes every molecule a scattering centre, reducing the mean free path spacing to a couple of atoms; the conductivity is correspondingly low.

We are not, of course, restricted to fully dense solids, making density ρ a possible variable after all. In fact, the best thermal insulators are porous materials – low-density foams, insulating fabric, cork, insulating wool, etc. – that take advantage of the low conductivity of still air trapped in the pores (λ for air is 0.02 W/m.K).

12.6 Design and manufacture: using thermal properties

Managing thermal stress Most structures, small or large, are made of two or more materials that are clamped, welded, or otherwise bonded together. This causes problems when temperatures change. Railway tracks will bend and buckle in exceptionally hot weather. Overhead transmission lines sag for the same reason — a problem for high-speed electric trains. Bearings seize, doors jam. Thermal distortion is a particular problem in precision measuring equipment and in the precise registration needed to fabricate computer chips.

All of these derive from *differential thermal expansion*, where the constraint between different materials generates *thermal stress*. As an example, many technologies involve coating materials with a thin surface layer of a different material to impart resistance to wear, corrosion, or oxidation. The coating is applied hot, and thermal stresses appear as it cools because of the difference in the expansion coefficients of the coating and substrate. The thermal stress is calculated as follows.

A thin film is bonded onto a much thicker component as in Figure 12.11(a). Imagine that the layer is detached as in Figure 12.11(b). A temperature drop of ΔT causes the layer to change in length by $\delta L_1 = \alpha_1 L_0 \Delta T$. Meanwhile, the substrate to which it was previously bonded contracts by $\delta L_2 = \alpha_2 L_0 \Delta T$. If $\alpha_1 > \alpha_2$, the surface layer shrinks more than the substrate. If we want to stick the film back on the much-more-massive substrate, covering the same surface as before, we must stretch it by applying the strain

$$\varepsilon = \frac{\delta L_1 - \delta L_2}{L_o} = \Delta T(\alpha_1 - \alpha_2)$$

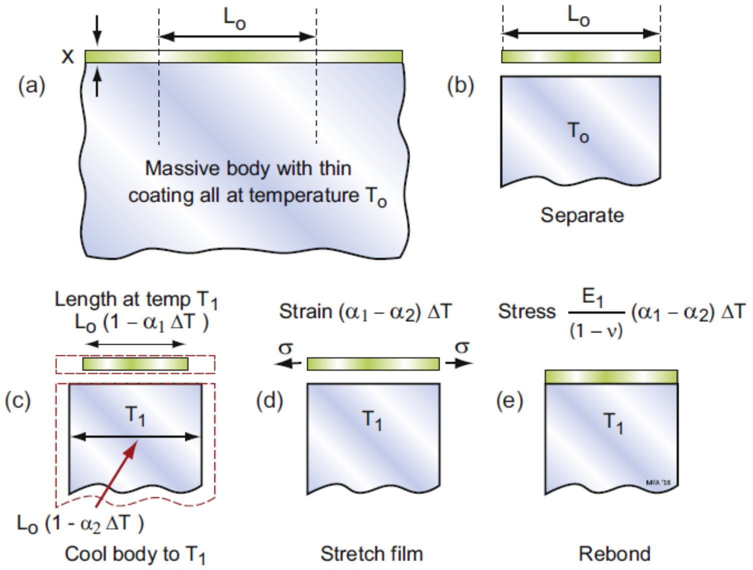

Figure 12.11 Thermal stresses in thin films arise on cooling or heating when the film and substrate have different expansion coefficients, α_1 in the film and α_2 in the substrate.

This requires a stress in the film of

$$\sigma_1 = \frac{E_1}{(1-\nu)} = (\alpha_1 - \alpha_2)\Delta T \qquad (12.11)$$

where Poisson's ratio ν enters because the stress state in the film is biaxial (see Chapter 4). The stress can be large enough to crack the surface film; the pattern of cracks seen on glazed tiles arises in this way. The way to avoid it is to avoid material combinations with very different expansion coefficients. The α–λ chart of Figure 12.4 has expansion α as one of its axes: benign choices are those that lie close together on this axis, while dangerous ones are those that lie far apart.

Avoiding materials with α mismatch is not always possible. Think of joining glass to metal – Pyrex to stainless steel, say – a common combination in high-vacuum equipment. Their expansion coefficients can be read from the α–λ chart of Figure 12.4: for Pyrex (borosilicate glass), $\alpha = 4 \times 10^{-6}$/K; for stainless steel, $\alpha = 20 \times 10^{-6}$/K – a big mismatch. Vacuum equipment has to be 'baked out' to desorb gases and moisture, requiring that it be heated to about 150°C, enough for the mismatch to crack the Pyrex. The answer is to grade the joint with one or more materials with expansion that lies between the two: first join the Pyrex to a glass of slightly higher expansion and the stainless steel to a metal of lower expansion – the chart suggests soda glass for the first and a nickel alloy for the second – and then diffusion-bond these to each other as shown in Figure 12.12. The graded joint spreads the mismatch, lowering the stress and the risk of damage.

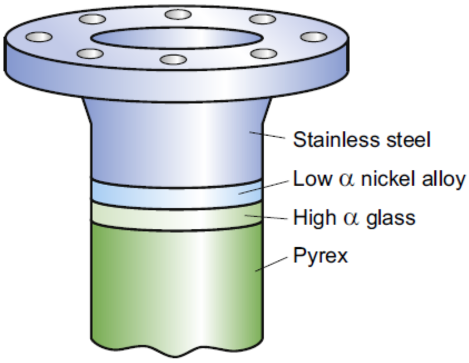

Figure 12.12 A graded joint.

There is an alternative, although it is not always practical. It is to put a compliant layer – rubber, for instance – in the joint; it is the way windows are mounted in cars. The difference in expansion is taken up by distortion in the rubber, transmitting very little of the mismatch to the glass or surrounding steel.

Thermal sensing and actuation Thermal expansion can be used to *sense* (to measure temperature change) and to *actuate* (to open or close valves or electrical circuits, for instance). The direct axial thermal displacement $\delta = \alpha L_o \Delta T$ is small; a *bi-material strip* is a way to magnify it, using bending. Two materials, now deliberately chosen to have different expansion coefficients α_1 and α_2, are bonded together in the form of a bi-material strip of thickness $2t$ as in Figure 12.13(a). When the temperature changes by $\Delta T = (T_1 - T_o)$, one expands more than the other, causing the strip to bend. The mid-thickness planes of each strip (dotted in Figure 12.13(b)) differ in length by $L_o(\alpha_2 - \alpha_1)\,\Delta T$. Simple geometry then shows that

$$\frac{R+t}{R} = 1 + (\alpha_2 - \alpha_1)\Delta T$$

from which

$$R = \frac{t}{(\alpha_2 - \alpha_1)\Delta T} \qquad (12.12)$$

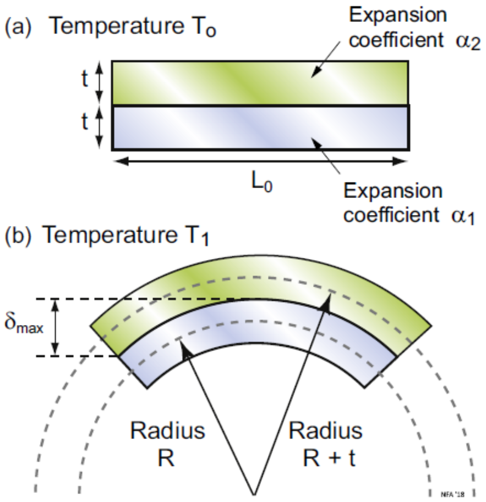

Figure 12.13 A bi-material strip.

The resulting upward displacement of the centre of the bi-material strip (assumed to be thin) is

$$\delta_{\max} = \frac{L_o^2}{8t}(\alpha_2 - \alpha_1)\Delta T \qquad (12.13)$$

A large aspect ratio L_o/t produces a large displacement that is linear in temperature.

Managing thermal distortion You don't need two materials to get thermal distortion: a *temperature gradient* will cause a component to distort even when it is made of just one. An originally flat plate with a temperature gradient between its surfaces will bend into a curve for the same reason that a bi-metallic strip does: because one side expands more than the other. Distortion due to thermal gradients is a problem in precision equipment in which heat is generated by the electronics, motors, actuators, or sensors necessary for their operation.

The answer is to make the equipment from materials with low expansion α (because this minimizes the expansion difference in a given temperature gradient) and with high conductivity λ (because this spreads the heat further, reducing the steepness of the gradient). The best choice is a material with high values for the ratio λ/α, shown as the diagonal contours on the chart of Figure 12.4. Materials with the most attractive values lie towards the bottom right. Diamonds are superb but perhaps impractical for other reasons. Copper, aluminium, silicon, aluminium nitride, and tungsten are good – they distort the least; stainless steel and titanium are significantly less good. Polymers are very poor.

Thermal shock resistance When thermal expansion is constrained, thermal stress appears. If the temperature of a component is changed abruptly by quenching it when hot into cold water, the surfaces are chilled almost instantly. It takes time for heat to be conducted out of the interior, so straight after quenching the bulk of the component is still hot. If the difference in temperature between the interior and the surface is ΔT, the difference in strain between them is $\varepsilon = \alpha \Delta T$. The surface is stuck to the interior, which constrains it, and thermal stress appears just as it did in the thin film of Figure 12.11. Complete constraint results in a surface stress of

$$\sigma = \frac{E}{(1 - v)} \alpha \Delta T \tag{12.14}$$

Superficially this looks the same as equation (12.11), but here only one material is involved. In ductile materials, the quenching stresses can cause yielding, permanent distortion, and residual stress; in brittle materials they can cause fracture. The ability of a material to resist fracture, its *thermal shock resistance* ΔT_s (units: K or °C), is the maximum sudden change in temperature to which such a material can be subjected without damage.

Transient heat flow problems The temperature distribution is static during steady-state heat flow and governed by Fourier's first law (equation (12.2)). When heat flow is transient, the distribution changes with time. Evaluating it (for heat conduction in one dimension) requires a solution for Fourier's second law,

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{a}\frac{\partial T}{\partial t} \tag{12.15}$$

with appropriate symmetry and boundary conditions (here t is time, x is distance, and a is the thermal diffusivity, as before). As an example, imagine a hot steel plate plunged into a tank of cold water (Figure 12.14). The heat diffuses outwards to the surfaces where it is removed by the water. If the plate is large in area compared to its thickness, the heat flow is one-dimensional and normal to the surface of the sheet, and the initial boundary conditions are $T = T_o$ at $x = 0$, and $T = T_1$ for all $x > 0$ (since initially we can regard the plate as semi-infinite). The solution to equation (12.15) for these conditions is

$$\frac{T - T_o}{T_1 - T_o} = erf\left(\frac{x}{2\sqrt{at}}\right) \tag{12.16}$$

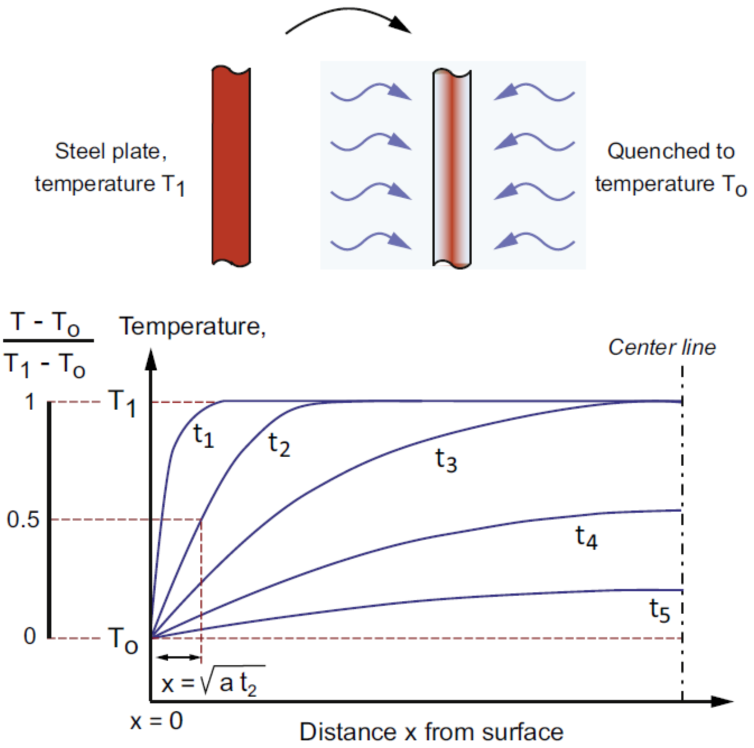

Figure 12.14 Quenching a steel plate – a transient heat flow problem. The temperature profile through the plate evolves with time.

The function *erf* (X) is called the error function. This equation predicts the temperature profiles, shown in the lower half of Figure 12.14, until $t \approx t_3$ (at which point cooling from both sides of the plate reaches the centre). For values of $X < 0.7$, the error function is approximately equal to its argument, meaning that *erf* $(X) \approx X$. The temperature profile immediately below the surface is then

$$\frac{T - T_o}{T_1 - T_o} = \left(\frac{x}{2\sqrt{at}}\right) \tag{12.17}$$

The temperature at a given depth x falls with time. The point at which the temperature has fallen to halfway between T_1 and T_o is found by setting equation (12.17) equal to 0.5, such that

$$x = \sqrt{at} \tag{12.18}$$

This distance is shown in Figure 12.14 for time $t = t_2$. As noted earlier, equation (12.18) is a particularly useful 'rule-of-thumb' for a characteristic distance of transient heat flow in time t. Here we derived it for quenching the surface of a semi-infinite plate, but it gives an approximate length-scale of heat diffusion in all transient problems.

For longer time-scales ($t = t_4$ or t_5), cooling from both faces of the sheet leads to a different solution to equation (12.15), which gives the temperature at mid-thickness for a plate of thickness ℓ as

$$\frac{T - T_o}{T_1 - T_o} = \frac{4}{\pi}\exp\left(-\frac{t}{(\ell^2/\pi^2\, a)}\right) \tag{12.19}$$

The temperature falls exponentially with time, with a characteristic time constant $t^* = (\ell^2/\pi^2 a)$. Note the similarity with equation (12.18); the characteristic cooling time scales with the distance (ℓ/π), about one-third the plate thickness.

Conduction with strength: heat exchangers A heat exchanger transfers heat from one fluid to another while keeping the fluids physically separated, as in power plants and the cooling systems of car and marine engines. Heat is transferred most efficiently if the wall separating the fluids is kept thin and the surface area large – a good solution is a tubular coil. At least one fluid is under pressure, so the wall must be strong enough to withstand it. Here there is a conflict in the design: thinner walls conduct heat faster, whereas thicker walls are stronger. Which material gives the best compromise?

Consider the idealized heat exchanger made of thin-walled tubes shown in Figure 12.15. The tubes have a given radius R and wall thickness t (which may be varied), and must support an internal pressure of p. The temperature difference between the fluids is ΔT. The objective is to maximize the heat transferred per unit surface area of tube wall. The heat flow-rate per unit area, q, is given by

$$q = -\lambda\frac{dT}{dx} = \lambda\frac{\Delta T}{t}\ \mathrm{W/m^2} \tag{12.20}$$

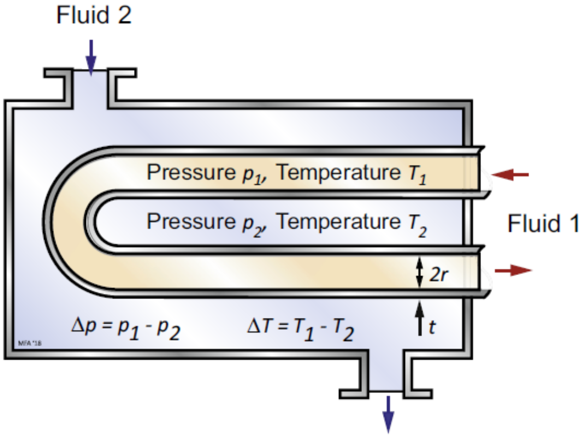

Figure 12.15 A heat exchanger.

The stress due to the internal pressure in a cylindrical thin-walled tube (Chapter 10, equation (10.7)) is

$$\sigma = p\,\frac{R}{t}$$

This stress must not exceed the yield strength σ_y for the material of which it is made, so the minimum thickness t needed to support the pressure difference p is

$$t = p\,\frac{R}{\sigma_y} \tag{12.21}$$

Combining equations (12.20) and (12.21) to eliminate the free variable t gives

$$q = \lambda\,\sigma_y\,\frac{\Delta T}{p\,R} \tag{12.22}$$

The best materials are therefore those with the highest values of the index $\lambda\sigma_y$. It is shown as a set of diagonal contours on the $\lambda-\sigma_y$ chart of Figure 12.6. The best materials for heat exchangers are those at the upper right of the figure: silver, copper, aluminium, and their alloys. All offer good corrosion resistance, but aluminium wins where cost and weight are to be kept low – in automotive radiators, for example. Marine heat exchangers use copper alloys even though they are heavier and more expensive because of their better corrosion resistance in seawater.

Insulation: thermal walls Before 1940 few people had central heating or air-conditioning. Now most have both, as well as fridges, freezers, and saunas. All consume power, and consuming power is both expensive and hard on the environment (Chapter 20). To save on both, it pays to insulate. Consider, as an example, the heated chamber (e.g. of a kiln) of Figure 12.16. The power lost per m^2 by conduction through its walls is

$$q = \lambda \frac{T_i - T_o}{t} \ \mathrm{W/m^2} \tag{12.23}$$

where t is the thickness of the insulation, T_o is the temperature of the outside, and T_i is the temperature of the inside. For a given wall thickness t the power consumption is minimized by choosing materials with the lowest possible λ. The chart of Figure 12.6 shows that these are foams, largely because they are about 95% gas and only 5% solid. Polymer foams are usable up to about 170°C; above this temperature, even the best of them lose strength and deteriorate. When insulating against heat then, an additional constraint must be met – that the material has a maximum service temperature $T_{\max}$ that lies above the planned temperature of operation. Metal foams are usable to higher temperatures but are expensive and – being metal – they insulate less well than polymers do. For high temperatures, ceramic foams are the answer. Low-density firebrick is relatively cheap, can operate up to 1000°C, and is a good thermal insulator. It is used for kiln and furnace linings.

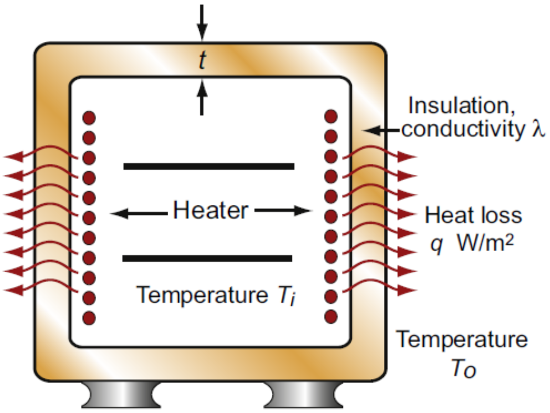

Figure 12.16 A heated chamber.

Using heat capacity: storage heaters The demand for electricity is greater during the day than at night. It is not economic for electricity companies to reduce output, so they seek instead to smooth demand by charging less for off-peak electricity. Storage heaters exploit this, using cheap electricity to heat a large block of material from which heat is later extracted by blowing air over it.

Storage heaters also fill other more technical roles. When designing supersonic aircraft or re-entry vehicles, it is necessary to simulate the conditions they encounter – hypersonic air flow at temperatures up to 1000°C. The simulation is done in wind tunnels in which the air stream is heated rapidly by passing it over a previously heated thermal mass before it hits the test vehicle, as in Figure 12.17. This requires a large mass of heat-storage material, and to keep the cost down the material must be cheap. The objective, both for the home heater and for the wind tunnel, is to store as much heat per unit cost as possible.

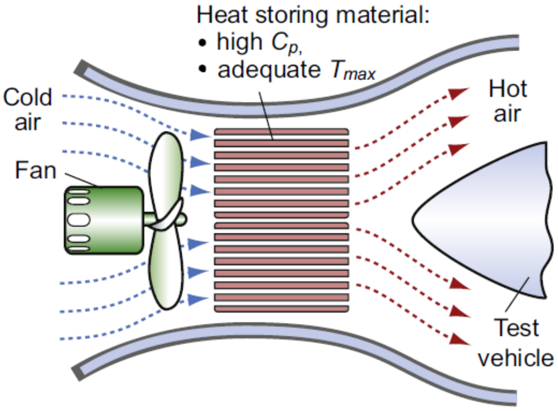

Figure 12.17 A wind tunnel with storage heating.

The energy stored in a mass m of material with a heat capacity C_p when heated through a temperature interval ΔT is

$$Q = m\, C_p\, \Delta T \tag{12.24}$$

The cost of mass m of material with a cost per kg C_m is

$$C = m\, C_m$$

Thus the heat stored per unit material cost is

$$\frac{Q}{C} = \frac{C_p}{C_m}\, \Delta T \tag{12.25}$$

For a given temperature interval ΔT, the best choice of material is simply that with the largest heat capacity, C_p, and lowest price, C_m. There is one other obvious constraint; the material must be able to tolerate the temperature to which it will be heated – say, $T_{\text{max}} > 150°\text{C}$ for the home heater, and $T_{\text{max}} > 1000°\text{C}$ for the wind tunnel. The best choice for the home heater is concrete that is cast to a shape that allows air flow. For the wind tunnel the best choice is refractory brick with air channels for rapid heat extraction.

Phase-change materials (PCMs): thermal buffers When a material vaporizes or melts or changes its crystal structure (all of which are known as 'phase changes'), they absorb or release heat – the *latent heat L* (J/kg) of the phase change – without changing temperature.

Suppose you want to keep something at a fixed temperature without external power. If the aim is to prevent the temperature of an object falling below a set value, it can be done by surrounding it with a liquid that solidifies at the temperature you want to maintain. As it solidifies it releases the latent heat of fusion, holding the temperature precisely at its solidification temperature (i.e. its melting point) until all the liquid is solid – it is the way some food warmers and 'back-woods' hand warmers work. The reverse is also practical: using the latent heat of melting to keep things cool. For this, choose a solid that melts, absorbing latent heat, at the temperature you want to maintain; 'cool bag' inserts for holiday travel work in this way. In both cases, change of phase is used as a *thermal buffer*.

Figure 12.18 shows two charts for selecting PCMs, one when the objective is to minimize mass, the other when it is to minimize volume.

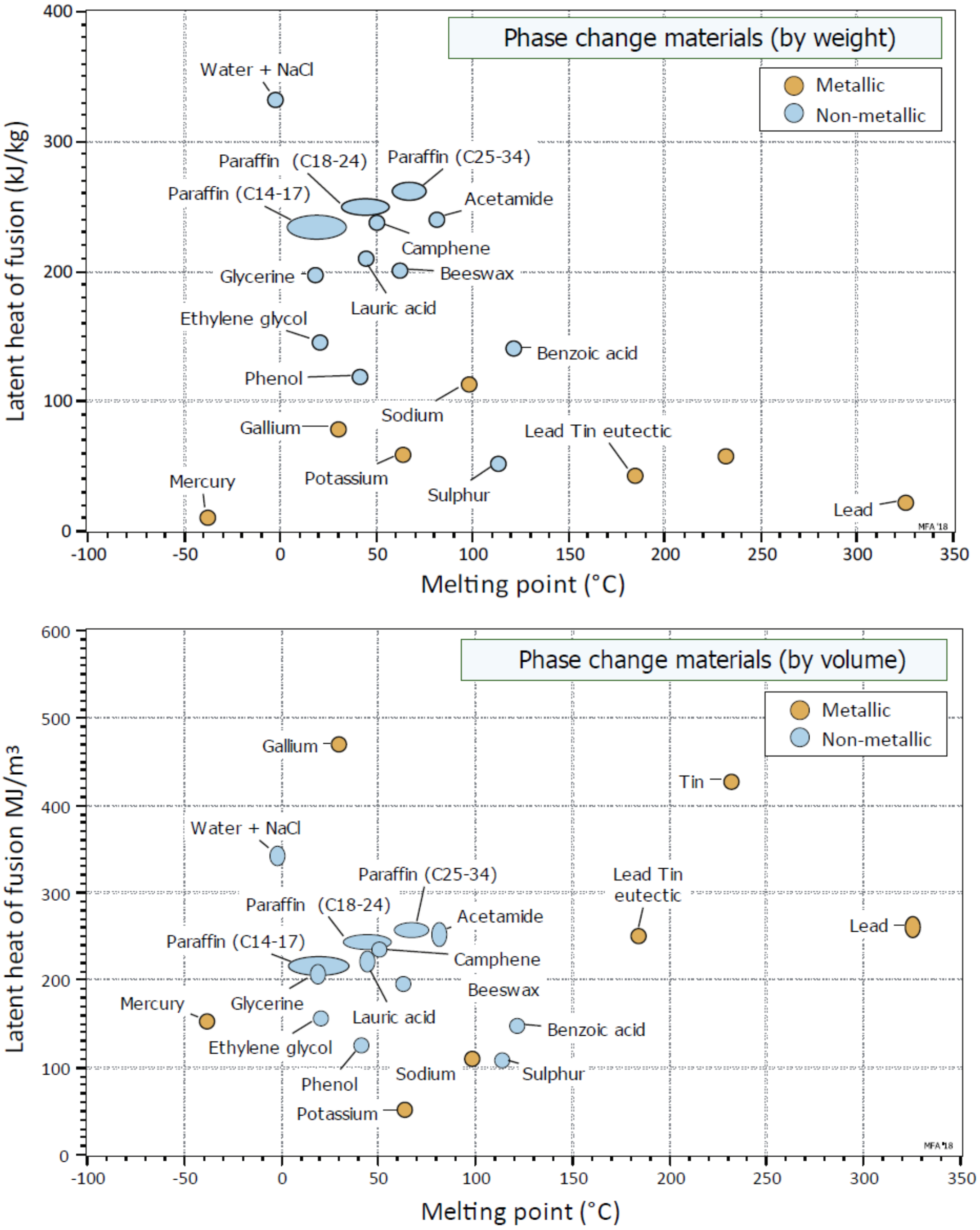

Figure 12.18 Phase change materials: latent heat by weight (above) and by volume (below).

Paraffin waxes (C_nH_{2n+2} with n between 14 and 34) and fatty acids have sharp melting points, have a large latent heat of melting, and are non-toxic and non-corrosive. Metals like gallium, lead, and tin, and eutectics like that of the lead–tin system have low latent heat per kg, but when compared per m^3, they perform exceptionally well. A large number of proprietary PCMs have been developed to cover the entire temperature range spanned by the figures, allowing selection that meets specific design requirements.

Shape-memory and super-elastic materials Almost all materials expand on heating and shrink on cooling. A few have a different response, one that comes from a solid-state phase change. *Shape-memory materials* are alloys based on titanium or nickel that can, while still solid, exist in two different crystal configurations with different shapes, called *allotropes*. If you bend the material, it progressively changes structure from one allotrope to the other, allowing large distortions. Shape-memory alloys have a critical temperature. If below this critical temperature, the distorted material stays in its new shape. Warm it up, and at its critical temperature, the structure reverts to the original allotrope and the sample springs back to its original shape. This has obvious application in fire alarms, sprinkler systems, and other temperature-controlled safety systems, and they are used for all of these.

But what if room temperature is already above this critical temperature? Then the material does not sit waiting for heat, but springs back to its original shape as soon as it is released, just as if it were elastic. The difference is that the phase change allows distortions that are larger, by a factor of 100 or more, than straightforward elasticity without phase change. The material is *super-elastic*. It is just what is needed for eyeglass frames that get sat on and otherwise mistreated, or springs that must allow very large displacements at a constant restoring force.

12.7 Summary and conclusions

All materials have:

- A specific heat, C_p – the amount of energy it takes to heat unit mass by unit temperature;
- A thermal expansion, α – the change in its dimensions with change of temperature;
- A thermal conductivity λ and thermal diffusivity a – the former characterising how fast heat is transmitted through the solid, the latter how long it takes for the temperature, once perturbed, to settle back to a steady pattern;

- Characteristic temperatures of changes of phase or behaviour – for a crystalline solid, its melting point T_m, and for non-crystalline solids, a glass transition temperature T_g – and also an empirical maximum service temperature $T_{\max}$, above which, for reasons of creep or degradation, continuous use is impractical;
- Latent heats of melting and of vaporisation – the energy absorbed at constant temperature when the solid melts or evaporates (and conversely, is released during solidification and condensation).

These properties can be displayed as material property charts – examples of which are utilised in this chapter. The charts illustrate the great range of thermal properties and the ways they are related. To explain these, we need an understanding of the underlying physics. The key concepts are that thermal energy is atomic-level vibration, that increasing the amplitude of this vibration causes expansion, and that the vibrations propagate as phonons, giving conduction. In metals the free electrons – the ones responsible for electrical conduction – also transport heat, and they do so more effectively than phonons, giving metals their high thermal conductivities. Thermal properties are manipulated by interfering with these processes: alloying to scatter phonons and electrons; and foaming to dilute the solid with low-conductivity, low-specific-heat gases.

The thermal response of a component to temperature change creates both problems and opportunities: thermal contraction can cause cracking or unwanted distortion; on the other hand, bi-material strips use controlled thermal distortion for actuation or sensing. It is the specific heat that makes an oven take 15 min to warm up, but it also stores heat in a way that can be recovered on demand. Good thermal conduction is not what you want in a coffee cup, but when it cools the engine of your car or the chip in your computer it is a big help. Thermal stresses and distortion are major issues in manufacturing too, from shaping processes to heat treatment and welding. And the transient cooling histories imposed, controlled by component geometry and the thermal diffusivity of the material, are central to understanding the evolution and control of the microstructure on which so many properties depend (Chapter 19).

This chapter has been about the thermal properties of materials. Heat, as we have said, also changes other properties, notably, strength. We look more deeply into that in Chapter 13.

13.1 Introduction and synopsis

Material properties change with temperature. Some do so in a simple linear way, easy to allow for in design: the density, the modulus, and the electrical conductivity are examples. But others, particularly the yield strength and the rates of oxidation and corrosion, change in more rapid and complex ways that can lead to disaster if not understood and allowed for in design.

This chapter explores the ways in which properties change with temperature and discusses design methods to deal with materials at high temperature. To do this we must first understand *diffusion*, the movement of atoms through solids, and the processes of *creep* and *creep fracture*, the continuous deformation of materials under load at temperature. Diffusion theory lies directly behind the analysis and procedures for high-temperature design with metals and ceramics. Polymers, being molecular, are more complicated in their creep behaviour, but semi-empirical methods allow safe design with these too. Diffusion and hot deformation also relate closely to material processing – forging, rolling, and heat treatment exploit the same physical mechanisms – so the chapter explores this too.

13.2 The temperature dependence of material properties

Linear and non-linear temperature dependence Some properties depend on temperature T in a linear way, meaning that

$$P \approx P_o\left(1 + \beta \frac{T}{T_m}\right) \tag{13.1}$$

where P is the value of the property, P_o its low-temperature value, and β is a constant. Figure 13.1 shows four examples: density, modulus, refractive index, and – for metals – electrical resistivity. Thus the density ρ and refractive index n decrease by about 6% on heating from cold to the melting point T_m ($\beta \approx -0.06$), the modulus E falls by a factor of 2 ($\beta \approx -0.5$), and the resistivity R increases by a factor of about 7 ($\beta \approx +6$). These changes cannot be neglected but are easily accommodated by using the value of the property at the temperature of the design.

Other properties are less forgiving. Strength falls in a much more sudden way and the rate of creep – the main topic here – increases exponentially (Figure 13.2). This we need to explore in more detail.

Viscous flow When a substance flows, its particles change neighbours; flow is a process of shear. Newton's law describes the flow rate in fluids under a shear stress τ:

$$\dot{\gamma} = \frac{\tau}{\eta}$$

where $\dot{\gamma}$ is the shear strain-rate and η the viscosity (units Pa.s). This is a linear relationship, like Hooke's law, with the modulus replaced by the viscosity and the strain by strain-rate (units/s). Viscous flow occurs at constant volume (Poisson's ratio = 0.5) and this means that problems of viscous flow can often be solved by taking the solution for elastic deformation and replacing

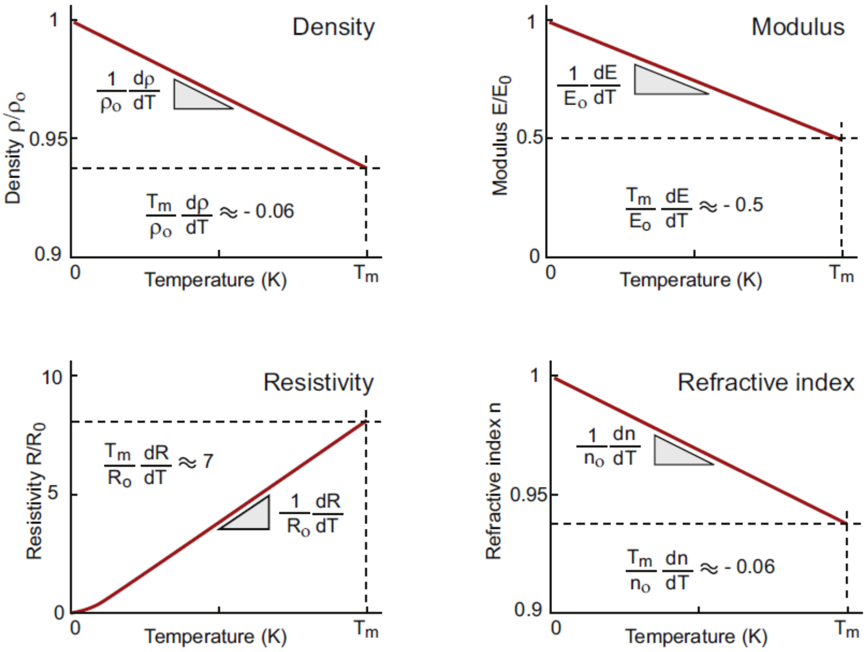

Figure 13.1 Linear dependence of properties on temperature: density, modulus, resistivity, and refractive index.

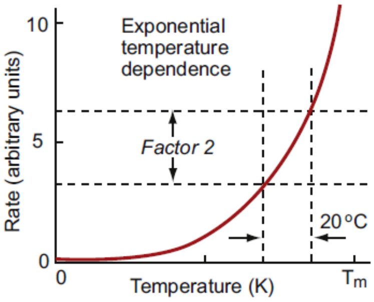

Figure 13.2 The exponential increase of rate with temperature.

the strain ε by the strain-rate $\dot{\varepsilon}$ and, using equation (4.10), Young's modulus E by 3η. Thus the rate at which a rod of a very viscous fluid, like tar, extends when pulled in tension is

$$\dot{\varepsilon} = \frac{\sigma}{3\eta} \tag{13.2}$$

The factor 1/3 appears because of the conversion from shear to normal stress and strain.

13.4 The science: diffusion

Creep deformation (and several other responses of materials at temperature) requires the relative motion of atoms. How does this happen, and what is its rate? To understand this, we go right down to the unit step – one atom changing its position relative to those around it, by *diffusion*.

Diffusion Diffusion is the spontaneous intermixing of atoms over time. In gases and liquids this is familiar – the spreading of smoke in still air, the dispersion of an ink-drop in water – and explained via the random motion and collisions of the atoms or molecules (Brownian motion). In crystalline solids the atoms are confined to lattice sites, but in practice they can still move and mix if they are warm enough.

Heat, as we have said, is atoms in motion. In a solid at temperature T they vibrate about their mean position with a frequency ν (about 10^{13} per second) with an average energy, kinetic plus potential, of $k_B T$ in each mode of vibration, where k_B is Boltzmann's constant (1.38×10^{-23} J/atom.K). This is the average, but at any instant some atoms have less, some more. Statistical mechanics gives the distribution of energies. The Maxwell–Boltzmann equation[1] describes the probability p that a given atom has an energy greater than a value q joules:

$$p = \exp - \left(\frac{q}{k_B T} \right) \tag{13.8}$$

Crystals, as we saw in Chapter 4, contain vacancies – occasional empty atom sites. These provide a way for diffusive jumps to take place. Figure 13.9 shows an atom jumping into a vacancy. To make such a jump, the atom marked in red (though it is the same sort of atom as the rest) must break away from its original comfortable site at A, its ground state, and squeeze between neighbours, passing through an activated state, to drop into the vacant site at B where it is once again comfortable. There is an energy barrier, q_m, between the ground state and the activated state to overcome if the atom is to move. The probability p_m that a given atom has thermal energy larger than this barrier is just equation (13.8) with $q = q_m$.

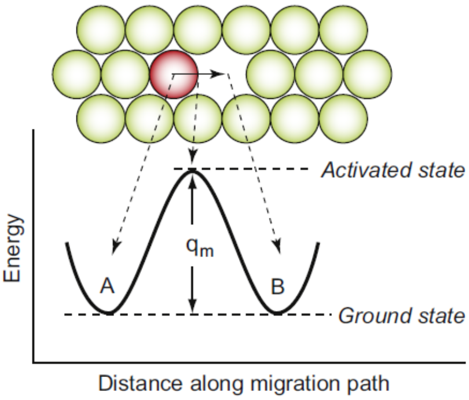

Figure 13.9 The energy change during a diffusive jump from site A to site B.

So, two things are needed for an atom to switch sites: enough thermal energy and an adjacent vacancy. A vacancy has an energy q_v, so – not surprisingly – the probability p_v that a given site be vacant is also given by equation (13.8), this time with $q = q_v$. Thus the overall probability of an atom changing sites is

$$p = p_v p_m = \exp - \left(\frac{q_v + q_m}{k_B T} \right) = \exp - \left(\frac{q_d}{k_B T} \right) \tag{13.9}$$

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[1] James Clerk Maxwell (1831–1879), pre-eminent Scottish theoretical physicist, considered by many to be the equal of Newton and Einstein (the latter kept a photo of Maxwell in his study, alongside pictures of Newton and Faraday). Maxwell's input to kinetic theory of diffusion was a relative sideshow compared to his electromagnetic theory, which unified the understanding at the time of electricity, magnetism, and optics.

where q_d is called the *activation energy for self-diffusion*. Diffusion, and phenomena whose rates are governed by diffusion, are often said to be *thermally activated*. If instead the red atom were chemically different from the green ones (so it is a substitutional solid solution), the process is known as *inter-diffusion*. Its activation energy has the same origin, but the barrier will have a different value. Interstitial solutes diffuse too: they have comfortable locations in their interstitial holes and need thermal activation to hop between them, but without the need for an adjoining vacancy (so in general their diffusion rates are much higher).

Figure 13.10 illustrates how mixing occurs by inter-diffusion. It shows a solid in which there is a concentration gradient dc/dx of red atoms: there are more in slice A immediately to the left of the central, shaded plane, than in slice B to its right. If atoms jump across this plane at random, there will be a net flux of red atoms to the right because there are more on the left to jump, and a net flux of white atoms in the opposite direction. The number in slice A, per unit area, is $n_A = 2r_o c_A$, and that in slice B is $n_B = 2r_o c_B$ where $2r_o$, the atom size, is the thickness of the slices and c_A and c_B are the concentration of red atoms on the two planes expressed as atom fractions. The difference is

$$n_A - n_B = 2r_o(c_A - c_B) = 4\,r_o^2\,\frac{dc}{dx}$$

(since $dc/dx = (c_A - c_B)/2r_o$). The number of times per second that an atom on slice A oscillates toward B, or one on B toward A, is $\nu/6$, since there are six possible directions in which an atom can oscillate in three dimensions, only one of which is in the right direction. Thus the net flux per second of red atoms across unit area from left to right is

$$J = -\,\frac{\nu}{6}\exp -\left(\frac{q_d}{k_B T}\right)4\,r_o^2\,\frac{dc}{dx}$$

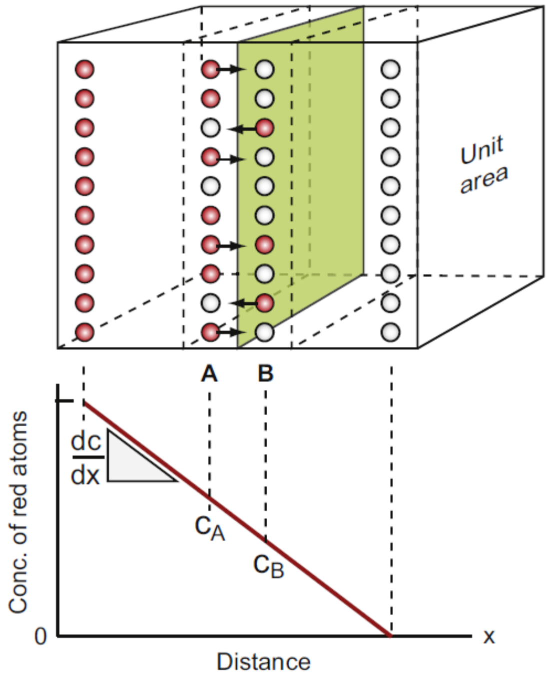

Figure 13.10 Diffusion in a concentration gradient.

It is usual to work with the activation energy per mole, Q_d, rather than that per atom, q_d, so we write $Q_d = N_A k_B$ and $R = N_A k_B$ (where N_A is Avogadro's number, 6.022×10^{23} mol^{-1}), and assemble the terms $4\nu r_o^2/6$ into a single *diffusion constant* D_o to give

$$J = -D_o \exp -\left(\frac{Q_d}{RT}\right) \frac{dc}{dx} \tag{13.10}$$

This is known as Fick's law:[2]

$$J = -D \frac{dc}{dx} \tag{13.11}$$

where D is called the *diffusion coefficient* given by

$$D = D_o \exp -\left(\frac{Q_d}{RT}\right) \tag{13.12}$$

Values for D_o and Q_d for lattice self-diffusion of elements are listed in Appendix A, Section A9. They have been measured experimentally for self-diffusion and diffusion of solutes for many alloys and ceramics. Most metals and ceramics are *polycrystalline* and are made up of grains, within which there are dislocations (Chapter 6). Grain boundaries and dislocations provide 'short-circuit' paths for faster diffusion because there is a bit more space between the atoms; these have their own values of D_o and Q_d.

Two rules of thumb are useful in making estimates of diffusion rates when data are not available. The first is that the activation energy for self-diffusion in kJ/mol, normalised by RT_m, is approximately constant for metals:

$$\frac{Q_d}{RT_m} \approx 18 \tag{13.13a}$$

The second is that the diffusion coefficient of metals, evaluated at their melting point, is also approximately constant:

$$D_{T_m} = D_o \exp -\left(\frac{Q_d}{RT_m}\right) \approx 10^{-12}\ \mathrm{m^2/s} \tag{13.13b}$$

Diffusion in liquids and non-crystalline solids The vacancies in a crystal can be thought of as *free volume* – free, because it is able to move, as it does when an atom jumps. The free volume in a crystal is thus in the form of discrete units, all of the same size – a size into which an atom with enough thermal energy can jump. Liquids and non-crystalline solids, too, contain free volume, but because there is no lattice or regular structure it is dispersed randomly between all the atoms or molecules. Experiments show that the energy barrier to atom movement in liquids is not the main obstacle to diffusion or flow. There is actually plenty of free volume among neighbours of any given particle, but it is of little use for particle jumps except when, by chance, it comes together to make an atom-sized hole – a temporary vacancy. This is a fluctuation problem like the Maxwell–Boltzmann problem and with a similar solution: diffusion in liquids is described by

$$D = \frac{2}{3} r_o^2 \nu \exp - \left(\frac{v_a}{v_f} \right) \tag{13.14}$$

where v_f is the average free volume per particle, v_a is the volume of the temporary vacancy, and r_o and ν have the same meaning as before.

Diffusion driven by other fields So far we have thought of diffusion driven by a concentration gradient. Concentration c is a *field quantity*; it has discrete values at different points in space (the concentration field). The difference in c between two nearby points divided by the distance between them defines the local concentration gradient, dc/dx.

Diffusion can be driven by other field gradients. A stress gradient, as we shall see in a moment, drives diffusional flow and power-law creep. An electric field gradient can drive diffusion in non-conducting materials. Even a temperature gradient can drive diffusion of matter as well as diffusion of heat.

Transient diffusion problems Fick's law for diffusion of matter, equation (13.11), captures the rate at which atoms flow down a uniform concentration gradient at steady state (i.e. when the concentration at a given position doesn't change with time). Fick's law is very like Fourier's law for steady-state heat flow, equation (12.2), and so, too, are the solutions for transient flow. Figure 13.11 shows two solid blocks of pure elements A and B that are brought into contact and heated. We will assume that A and B form a solid solution in one another in any proportions, as do copper and nickel, for example. The concentration profile evolves with time, heading (at very long times) to a uniform mixture of 50% A atoms to 50% B atoms. The concentration profiles resemble the temperature profiles as heat diffuses out of a hot plate after quenching (Figure 12.14). Let's explore why.

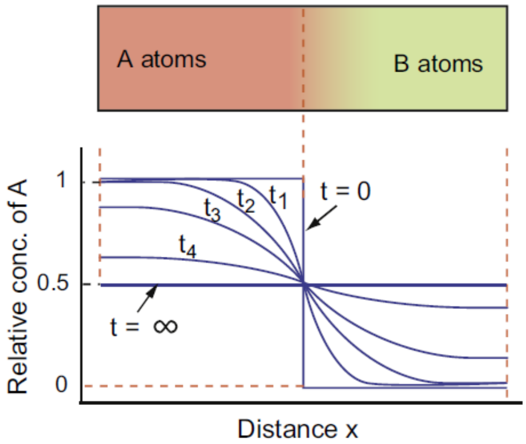

Figure 13.11 Intermixing by diffusion.

Consider the flux of atoms in and out of a small volume element at a given value of x. The flux of diffusing atoms is proportional to the local concentration gradient, equation (13.11), so in a small time step δt, a slightly different number of atoms enter and leave the volume element, reflecting the small difference in the concentration on either side. The concentration of the element will therefore change by δC, just as the temperature changed a little in transient heat flow because of a difference in heat entering and leaving a volume element. The differential equation describing the change in concentration C with position x and time t, when atoms are diffusing in one dimension (the x-direction), is

$$\frac{\partial^2 C}{\partial x^2} = \frac{1}{D}\frac{\partial C}{\partial t} \tag{13.15}$$

(where the curly '∂' again signifies that this is a partial differential equation). This is the same as the heat-flow equivalent (equation (12.15)) with concentration C replacing temperature T and the diffusion coefficient D replacing the thermal diffusivity, a, so the solution for one is easily adapted for the other.

Look at the left half of Figure 13.11. At time $t = 0$ the relative concentration of A atoms is uniform and equal to 1; that of B is zero. The successive concentration profiles at times t_1, t_2, t_3, t_4 evolve between these limits, just as the temperature in Figure 12.15 started at T_1 and eventually settled to T_o. At short times, the profile is described by the error function, erf(X), as in equation (12.16), which simplifies at short times to equation (12.17). We therefore anticipate that there will be a characteristic atom diffusion distance for a time t, given by

$$x \approx \sqrt{Dt} \tag{13.16}$$

relating the time and depth at which the concentration has fallen halfway between its initial and final value (i.e. 0.75 in the left half and 0.25 in the right half). These solutions apply directly to many problems in materials processing, and a number are presented next.

Diffusion in surface hardening of steel: carburising Many steels are used in applications in which the surfaces are in sliding or rolling contact, placing greater demands on surface properties than on those of the interior. To cope with this, *surface engineering* techniques are used to selectively enhance surface properties. One method is *carburising* – diffusing carbon into the surface of a hot steel component, locally increasing the concentration to that of an alloy that is 5 times or more harder, greatly improving the resistance to wear (Chapter 11). Figure 13.12 shows the concentration profile for carburising a steel of carbon concentration C_o. The carburised layer is thin compared to the component dimensions making this a semi-infinite problem with one-dimensional diffusion. If the surface concentration is maintained at C_s, the concentration profile $C(x, t)$ is

$$C(x,t) = C_o + (C_s - C_o)\left(1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right) \tag{13.17}$$

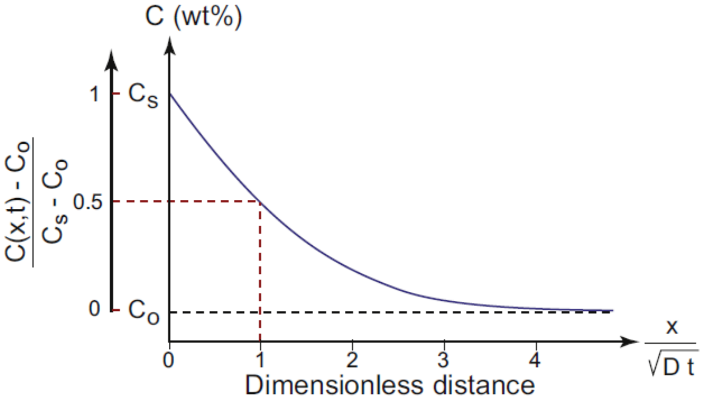

Figure 13.12 Concentration profile of carbon in iron during surface carburising.

In this case the solution includes $(1 - \mathrm{erf}(X))$, as the curves fall with increasing x, while the factor $(C_s - C_o)$ scales the function to match the boundary conditions. Rearranging equation (13.17), we get a simple dimensionless solution:

$$\left(\frac{C(x,t) - C_o}{C_s - C_o}\right) = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{13.18}$$

Figure 13.12 has these dimensionless quantities as axes, scaling the depth x with the characteristic diffusion distance $\sqrt{Dt}$. The depth at which the concentration has increased to a value halfway between C_o and C_s is shown – it is simply $x = \sqrt{Dt}$. Let's use the solution to estimate the timescale of a typical carburising treatment.

Diffusion in doping of semiconductors Semiconductors achieve their unusual electrical properties by doping high-purity silicon with low concentrations of atoms such as boron and phosphorus. One way to do this is to diffuse in a controlled quantity of boron atoms at the surface – 'pre-deposition' – and then to remove the source of boron and to 'drive in' the dopant to a much greater depth. Figure 13.13 illustrates the concentration profiles after these two steps. The area under the two curves is the same, being the total number of B atoms diffused in during pre-deposition. In the first stage, the profile is the same as that for carburising. The mathematical solution for the drive-in stage takes a different form because the surface concentration C_s now changes with time, but the extent of the distributions of solute can still be estimated for both stages using $x = \sqrt{Dt}$, with the relevant values for D and t in each case (as shown in Figure 13.13).

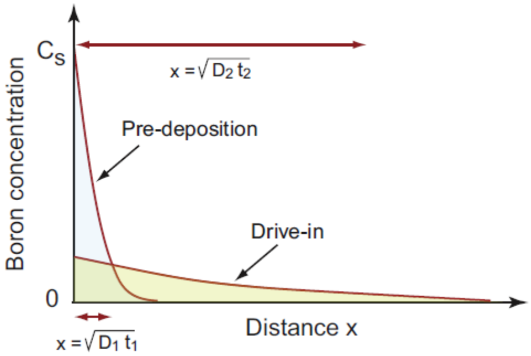

Figure 13.13 Concentration profile of boron in silicon during pre-deposition and drive-in.