48.1 Introduction and synopsis

Stress causes strain. If you are human, the ability to cope with stress without undue strain is called *resilience*. If you are a material, it is called *elastic modulus*.

Stress is something that is applied to a material by loading it. Strain e a change of shape e is its response. The strain depends on the material, on the magnitude of the stress and the way it is applied e the *mode of loading*. The cover picture illustrates the common modes of loading. Ties carry tension e often, they are cables. Columns carry compression e often they are hollow tubes. Beams carry bending moments, like the wing spar of the plane or the horizontal roof beams of the airport. Shafts carry torsion, as in the drive shaft of cars or the propeller shaft of the plane. Pressure vessels contain a pressure, as in the tires of the plane.

Stiffness is the resistance to elastic shape change, 'elastic' meaning that the material returns to its original shape when the stress is removed. *Strength* (Chapter 6) is its resistance to permanent distortion or total failure. Stress and strain are not material properties; they describe a stimulus and a response. Stiffness (measured by the elastic modulus E, defined in a moment) and strength (measured by the elastic limit s_y or tensile strength s_{ts}) *are* material properties. Stiffness and strength are central to mechanical design, often in combination with the density, r. This chapter introduces stress and strain and the elastic moduli that relate them. These properties are neatly summarised in a *material property chart* e the moduluseedensity chart e the first of many that we shall explore in this book.

Density and modulus are *microstructure-insensitive properties*. They derive directly from the atomic weight and packing, and from the nature of the bonds that bind the atoms of the material together. This distinguishes them (and a number of other such properties) from *microstructure-sensitive properties* like strength and toughness that depend strongly on the way that the material has been processed. In this chapter, we explore atomic bonding and packing, giving insight into the way modulus and density vary across the rows of the periodic table of the elements and the way they change when elements are combined to form ceramics, glasses, polymers and elastomers. There is not much you can do to change the weight, packing and bonding of atoms, but there are two ways in which modulus and density *can* be manipulated: by combining two materials together to make a composite, or by dispersing space within them, making foams. Property charts are a good way to show how this works.

48.2 Density, stress, strain and elastic moduli

Density Many applications (e.g. aerospace components, automotive bodies, sports equipment) require stiffness and strength at low weight, and this depends in part on the density of the materials of which they are made. Density is mass per unit volume, measured in kg/m^3.

The density of samples with regular shapes can be determined using a precision mass balance and accurate measurements of the dimensions (to give the volume), but this is not the best way. Better is the 'double weighing' method: the sample is first weighed in air and then, when fully immersed, in a liquid of known density. When immersed, the sample feels an upward force equal to the weight of liquid it displaces (Archimedes' principle[1]). The density is then calculated, as shown in Figure 4.1.

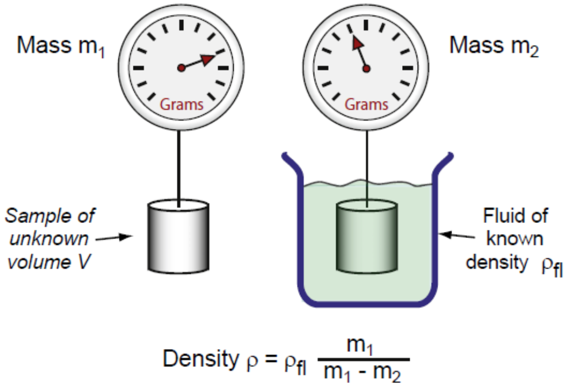

Figure 4.1 Measuring density.

Modes of loading Most engineering components carry loads. Their elastic response depends on the way the loads are applied. As explained earlier, the components in both structures shown on the front page of this chapter are designed to withstand different modes of loading: tension, compression, bending, torsion and internal pressure. Usually one mode dominates, and the component can be idealised as one of the simply loaded cases in Figure 4.2 e *tie, column, beam, shaft* or *shell*. Ties carry simple axial tension, shown in (a); columns do the same in simple compression, as in (b). Bending of a beam (c) creates simple axial tension in elements on one side of the neutral axis (the centre-line, for a beam with a symmetric cross- section) and simple compression in those on the other. Shafts carry twisting or torsion (d), which generates shear rather than axial load. Pressure difference applied to a shell, like the cylindrical tube shown in (e), generates bi-axial tension or compression.

Stress Consider a force F applied normal to the face of an element of material, as in Figure 4.3 on the left of row (a). The force is transmitted through the element and balanced by an equal but opposite force on the other side, so that it is in equilibrium (it does not move). Every plane normal to F carries the force. If the area of such a plane is A, the *tensile stress* **S** in the element (neglecting its own weight) is

$$\sigma = \frac{F}{A}$$

---

[1] Archimedes (287e212 BC), Greek mathematician, engineer, astronomer and philosopher, designer of war machines, the Archimedean screw for lifting water, evaluator of p (as 3 1/7) and conceiver, while taking a bath, of the principle that bears his name.

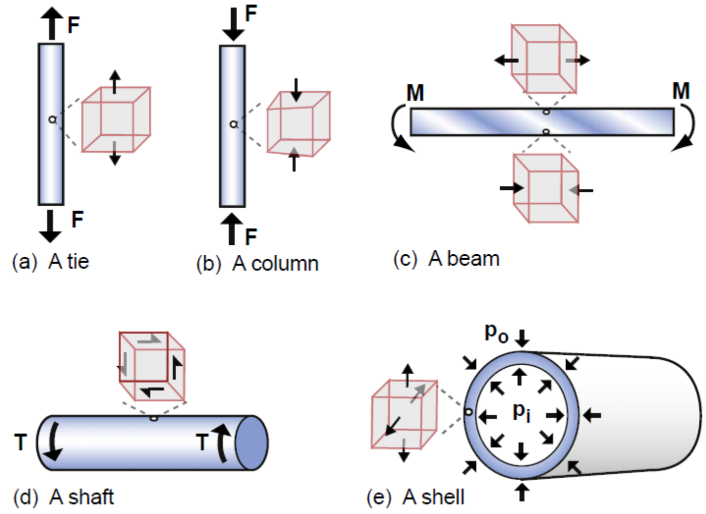

Figure 4.2 Modes of loading and states of stress.

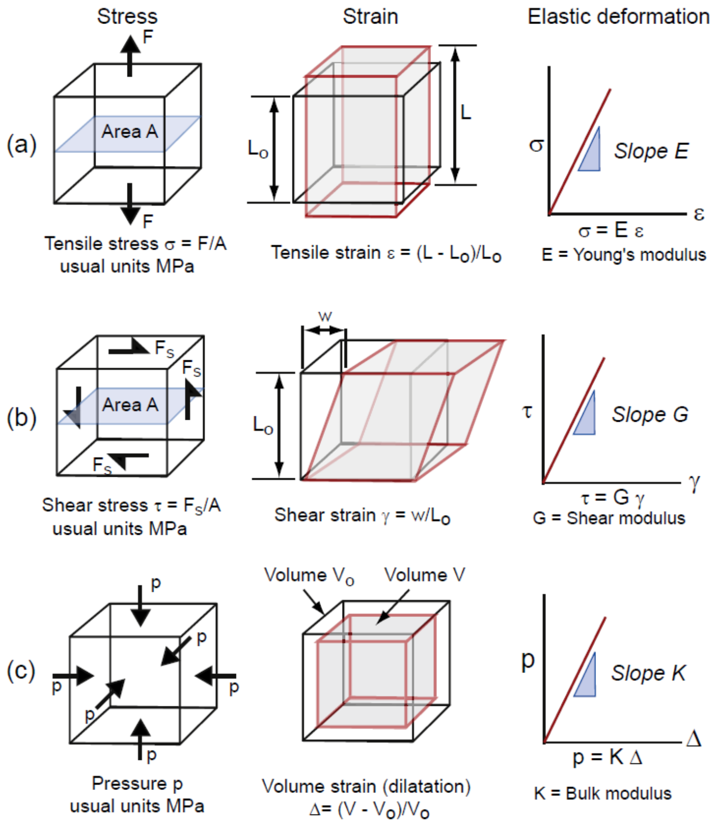

Figure 4.3 The definitions of stress, strain and elastic moduli.

If the sign of F is reversed, the stress is compressive and given a negative sign. Forces[2] are measured in newtons (N), so stress has the dimensions of N/m^2. But a stress of 1 N/m^2 is tiny e atmospheric pressure is 10^5 N/m^2 e so the usual unit is MN/m^2 (10^6 N/m^2), called *mega- pascals*, symbol[3] MPa.

If, instead, the force lies parallel to the face of the element, three other forces are needed to maintain equilibrium: an equal and opposite force on the opposing face, for force equilibrium, and a complementary pair of forces on the other two faces, for moment equilibrium (Figure 4.3, row (b)). This creates a state of *pure shear* in the element. The shaded plane, for instance, carries the *shear stress* τ of

$$\tau = \frac{F_S}{A}$$

The units, as before, are MPa.

One further state of multi-axial stress is useful in defining the elastic response of materials: that produced by applying equal tensile or compressive forces to all six faces of a cubic element, as in Figure 4.3, row (c). *Any* plane in the cube now carries the same state of stress e it is equal to the force on a cube face divided by its area. The state of stress is one of *hydrostatic pressure*, symbol p, again with the units of MPa. There is an unfortunate convention here. Pressures are positive when they push e the reverse of the convention for simple tension and compression.

---

[2] Isaac Newton (1642e1727), scientific genius and alchemist, formulator of the laws of motion, the inverse-square law of gravity (though there is some controversy about this), laws of optics, the differential calculus and much more.

[3] Blaise Pascal (1623e1662), philosopher, mathematician and scientist, who took a certain pleasure in publishing his results without explaining how he reached them. Almost all, however, proved to be correct.

Engineering components can have complex shapes and can be loaded in different ways, creating complex distributions of stress. But no matter how complex, the stresses in any small element within the component can always be described by a combination of tension, compression and shear. Commonly, the simple cases of Figure 4.3 suffice, using superposition of two cases to capture, for example, bending plus compression.

Strain Strain is the response of materials to stress (second column of Figure 4.3). A tensile stress σ applied to an element causes the element to stretch. If the element in Figure 4.3(a), originally of side length L_o, stretches by $\delta L = L - L_o$, the nominal *tensile strain* is

$$\varepsilon = \frac{\delta L}{L_o} \tag{4.3}$$

A compressive stress shortens the element; the nominal compressive strain (negative) is defined in the same way. Since strain is the ratio of two lengths, it is dimensionless.

A shear stress causes a *shear strain* γ (Figure 4.3(b)). If the element shears by a distance w, the shear strain is

$$\tan(\gamma) = \frac{w}{L_o} = \gamma \tag{4.4}$$

In practice, $\tan\gamma \approx \gamma$ because elastic strains are almost always small. Finally, a hydrostatic pressure p causes an element of volume V to change in volume by δV. The volumetric strain, or *dilatation* (Figure 4.3(c)), is

$$\Delta = \frac{\delta V}{V} \tag{4.5}$$

Stress–strain curves and moduli Figure 4.4 shows typical tensile stress–strain curves for a ceramic, a metal and a polymer, each taken all the way to failure. The initial part, up to the *elastic limit* σ_{el}, is approximately linear (Hooke's[4] law), and it is elastic, meaning that the strain is recoverable – the material returns to its original shape when the stress is removed. Stresses above the elastic limit cause permanent deformation (ductile behaviour) or brittle fracture.

Within the linear elastic regime, strain is proportional to stress (Figure 4.3, third column). The tensile strain is proportional to the tensile stress:

$$\sigma = E\varepsilon \tag{4.6}$$

and the same is true in compression. The constant of proportionality, E, is *Young's[5] modulus*. Similarly, the shear strain γ is proportional to the shear stress τ:

$$\tau = G\gamma \tag{4.7}$$

---

[4] Robert Hooke (1635–1703), able but miserable man, inventor of the microscope, and perhaps, too, of the idea of the inverse-square law of gravity. He didn't get along with Newton.

[5] Thomas Young (1773–1829), English scientist, expert on optics and deciphering ancient Egyptian hieroglyphs (among them, the Rosetta stone). It seems a little unfair that the modulus carries his name, not that of Hooke.

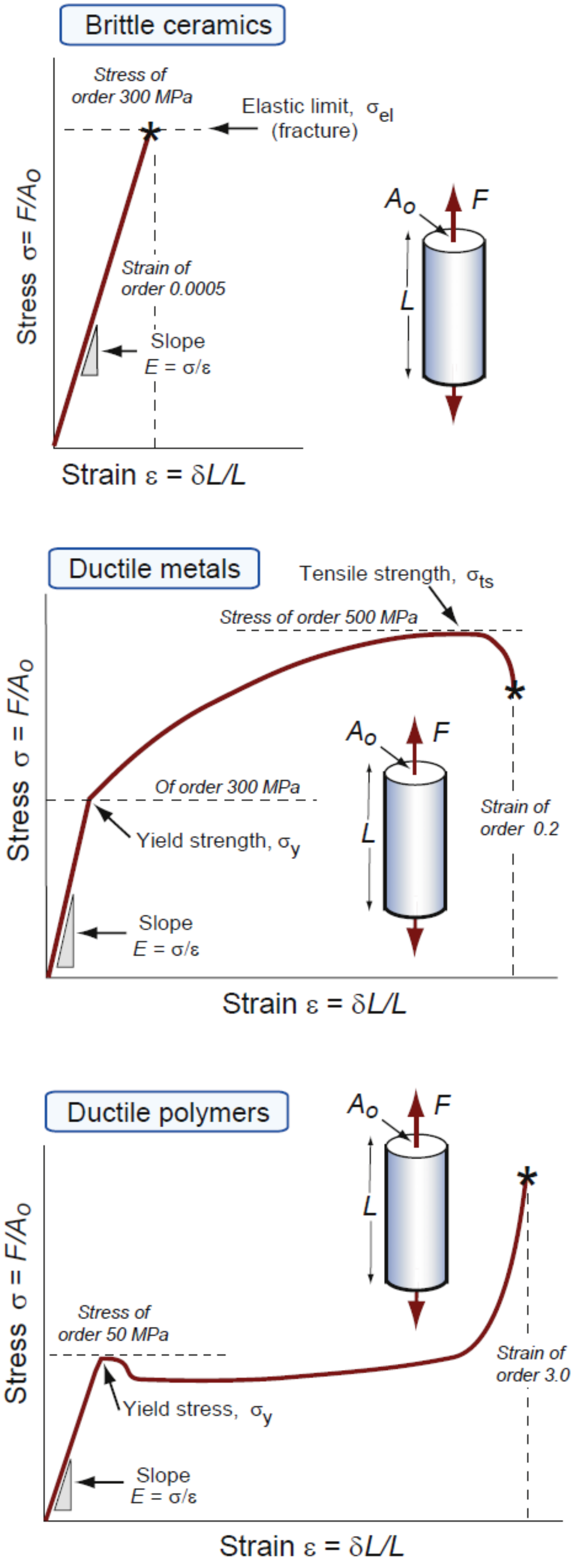

Figure 4.4 Tensile stress–strain curves for ceramics, metals and polymers.

and the dilatation Δ is proportional to the pressure p:

$$p = K\Delta \tag{4.8}$$

where G is the *shear modulus* and K the *bulk modulus*, as illustrated in the third column of Figure 4.3. All three of these moduli have the same dimensions as stress, that of force per unit area (N/m^2 or Pa). As with stress, it is convenient to use a larger unit, this time an even bigger one, that of 10^9 N/m^2, *gigapascals*, or GPa.

Young's modulus, the shear modulus and the bulk modulus are related, but to relate them we need one more quantity, *Poisson's*[6] *ratio*. When stretched in one direction, the element of Figure 4.3(a) generally contracts in the other two directions, as it is shown doing here. Poisson's ratio, ν, is the negative of the ratio of the lateral or transverse strain, ε_t, to the axial strain, ε, in tensile loading:

$$\nu = -\frac{\varepsilon_t}{\varepsilon} \tag{4.9}$$

Since the transverse strain itself is negative, ν is positive – it is typically about 1/3.

In an isotropic material (one for which the moduli do not depend on the direction in which the load is applied), the moduli are related in the following ways:

$$G = \frac{E}{2(1+\nu)}; \quad K = \frac{E}{3(1-2\nu)} \tag{4.10}$$

Commonly, $\nu \approx 1/3$ so that

$$G = \frac{3}{8}E \quad \text{and} \quad K = E \tag{4.11a}$$

---

[6] Siméon Denis Poisson (1781–1840), French mathematician, known both for his constant and his distribution. He was famously uncoordinated, failed geometry at university because he could not draw, and had to abandon experimentation because of the disasters resulting from his clumsiness.

Elastomers are exceptional. For these, $\nu \approx 1/2$ when

$$G = \frac{1}{3}E \quad \text{and} \quad K \gg E \tag{4.11b}$$

This means that rubber (an elastomer) is easy to stretch in tension (low E), but if constrained from changing shape, or loaded hydrostatically, it is very stiff (large K) – a feature for which designers of shoes must allow.

Hooke's law in three dimensions The simple loading states in Figure 4.2 lead to stresses in one or two perpendicular directions. But, as we have now seen, even under uniaxial load, the strain is inherently three-dimensional, thanks to Poisson's ratio. So it is helpful to relate stress and strain in a more general way that allows for loading acting in all three perpendicular directions at once.

Figure 4.5 shows the cubic element of material, now subjected to three unequal stresses σ_1, σ_2 and σ_3, resulting in strains ε_1, ε_2 and ε_3. To relate stress to strain, we use the principle of superposition – applying each stress in turn, finding the strains and then summing these to find the overall strain when all three stresses act together. First applying a stress σ_1, the resulting strains (from equations (4.6) and (4.9)) are

$$\varepsilon_1 = \frac{\sigma_1}{E}, \quad \varepsilon_2 = \varepsilon_3 = -\nu\varepsilon_1 = \frac{\nu\sigma_1}{E} \tag{4.12}$$

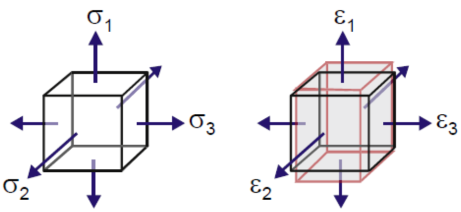

Figure 4.5 Multi-axial states of stress and strain.

Repeating for stresses σ_2 and σ_3, and summing the strains gives us *Hooke's law in three dimensions*:

$$\begin{aligned} \varepsilon_1 &= \frac{1}{E}(\sigma_1 - \nu\sigma_2 - \nu\sigma_3) \\ \varepsilon_2 &= \frac{1}{E}(-\nu\sigma_1 + \sigma_2 - \nu_3) \\ \varepsilon_3 &= \frac{1}{E}(-\nu\sigma_1 - \nu\sigma_2 + \sigma_3) \end{aligned} \tag{4.13}$$

These results are particularly helpful in design problems in which strain is constrained. Figure 4.6 shows a cube of material located in a rigid slot of the same width as the cube. A vertical downwards stress $\sigma_1 = -\sigma$ is applied to the top face of the cube. At first sight, this looks like conventional uniaxial compression. But the cube wishes to expand laterally due to Poisson's ratio. In the 2-direction it can do so, but perpendicular to the slot it is constrained; the strain in the 3-direction is zero. What does Hooke's law tell us about the stresses and strains?

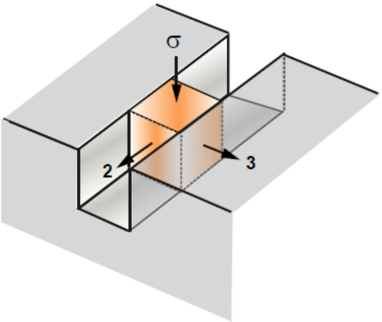

Figure 4.6 Constrained compression.

For the 3-direction, we can write (noting that $\sigma_2 = 0$).

$$\varepsilon_3 = 0 = \frac{1}{E}(+\nu\sigma + \sigma_3), \quad \text{so } \sigma_3 = -\nu\sigma$$

The effect of constraint is therefore to induce a compressive stress $\nu\sigma$ in the constrained direction, perpendicular to the applied stress. But this stress will itself contribute a Poisson strain in the 1-direction, so the strain vertically is

$$\varepsilon_1 = \frac{1}{E}(\sigma_1 - \nu\sigma_3) = \frac{-\sigma}{E}(1 - \nu^2)$$

Now look at the ratio of stress to strain in the 1-direction:

$$\frac{\sigma_1}{\varepsilon_1} = \frac{E}{(1 - \nu^2)} \tag{4.14}$$

The constrained cube behaves like a material with an 'effective modulus' which is greater than E (since the factor $(1 - \nu^2)$ is less than unity).

The effect is even more marked when there is constraint in both 2- and 3-directions (see Exercises at the end of the chapter), and the effect is most significant for values of Poisson's ratio near 0.5. As noted earlier, the solid material with the lowest modulus – rubber – displays the most significant stiffening effect when it is loaded in a geometry that imposes constraint.

Elastic energy If you stretch an elastic band, energy is stored in it. The energy can be considerable: catapults can be lethal; the elastic deflection of truck springs can cushion the truck and its contents. The super-weapon of the Roman arsenal at one time was a wind-up mechanism that stored enough elastic energy to hurl a 10-kg stone projectile 100 m.

How do you calculate this energy? A force F acting through a displacement dL does work FdL. A stress $\sigma = F/A$ acting through a strain increment $d\varepsilon = dL/L$ does work per unit volume

$$dW = \frac{FdL}{AL} = \sigma d\varepsilon \tag{4.15}$$

with units of J/m^3. If the stress is acting on an elastic material, this work is stored as elastic energy. The elastic part of all three stress–strain curves of Figure 4.4 – the part of the curve before the elastic limit – is linear; in it, $\sigma = E\varepsilon$. The work done per unit volume as the stress is raised from zero to a final value σ^* is the area under the stress–strain curve:

$$W = \int_0^{\sigma^*/E} \sigma d\varepsilon = \frac{1}{2}\frac{(\sigma^*)^2}{E} \tag{4.16}$$

This is the energy that is stored, per unit volume, in an elastically strained material. The energy is released when the stress is relaxed.

Measurement of Young's modulus You might think that the way to measure the elastic modulus of a material would be to apply a small stress (to be sure to remain in the linear elastic region of the stress–strain curve), measure the strain and divide one by the other. In reality, moduli measured as slopes of stress–strain curves are inaccurate, often by a factor of two or more, because of contributions to the strain from material creep or deflection of the test machine. Accurate moduli are measured dynamically: by measuring the frequency of natural vibrations of a beam or wire, or by measuring the velocity of sound waves in the material. Both depend on $\sqrt{E/\rho}$, so if you know the density ρ, you can calculate E.

Stress-free strain Stress is not the only stimulus that causes strain. Some materials respond to a magnetic field by shrinking – an effect known as magnetostriction. Others respond to an electrostatic field in the same way – they are known as piezo-electric materials. In each case, a material property relates the magnitude of the strain to the intensity of the stimulus (Figure 4.7). The strains are small, but the stimulus can be controlled with great accuracy, and the material response is extremely fast. Magnetostrictive and piezo-electric strain can be driven at high frequency. This is exploited in precision positioning devices, acoustic generators and sensors – applications we return to in Chapters 15 and 16.

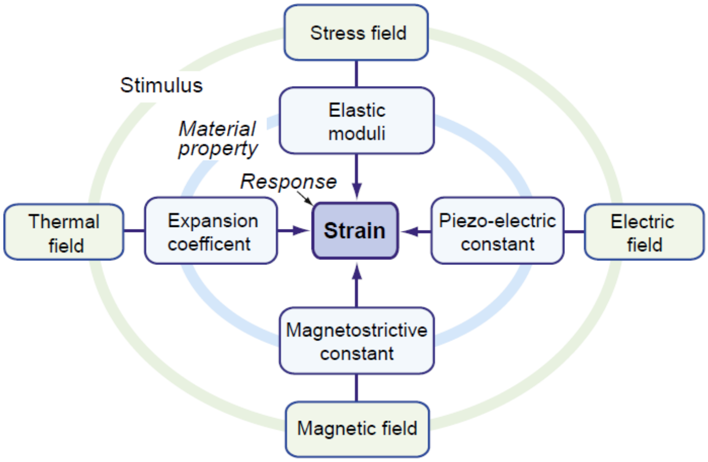

Figure 4.7 Stimuli, material properties and response.

A more familiar effect is that of thermal expansion: strain caused by change of temperature. The thermal strain ε_T is linearly related to the temperature change ΔT by the *expansion coefficient*, α:

$$\varepsilon_T = \alpha \Delta T \tag{4.17}$$

where the subscript T is a reminder that the strain is caused by temperature change, not by stress.

The term 'stress-free strain' is a little misleading. It correctly conveys the idea that the strain is not *caused* by stress but by something else. But these strains can nonetheless give rise to stresses if the body suffering the strain is constrained. Thermal stress, arising from constrained thermal expansion, can be a particular problem, causing mechanisms to jam and railway tracks to buckle. We analyse it in Chapter 12.

4.3 The big picture: material property charts

If we want materials that are stiff and light, we need an overview of what's available. That is the role of material property charts (introduced in Chapter 2).

The modulus–density chart The moduli and densities of common engineering materials are plotted in Figure 4.8; material families are enclosed in coloured envelopes. The modulus E spans seven decades[7], from 0.0001 to nearly 1000 GPa; the density ρ spans a factor of 2000, from less than 10 to 20,000 kg/m^3. Ceramics (yellow envelope) and metals (red envelope) have high moduli and densities; none has a modulus less than 10 GPa or a density less than 1700 kg/m^3. Polymers, by contrast, all have moduli below 10 GPa and densities that are lower than those of any metal or ceramic – most are close to 1000 kg/m^3 (the density of water). Elastomers have roughly the same density as other polymers, but their moduli are lower by a further factor of 100 or more. Materials with even lower densities are porous: synthetic foams and natural cellular structures like wood and cork.

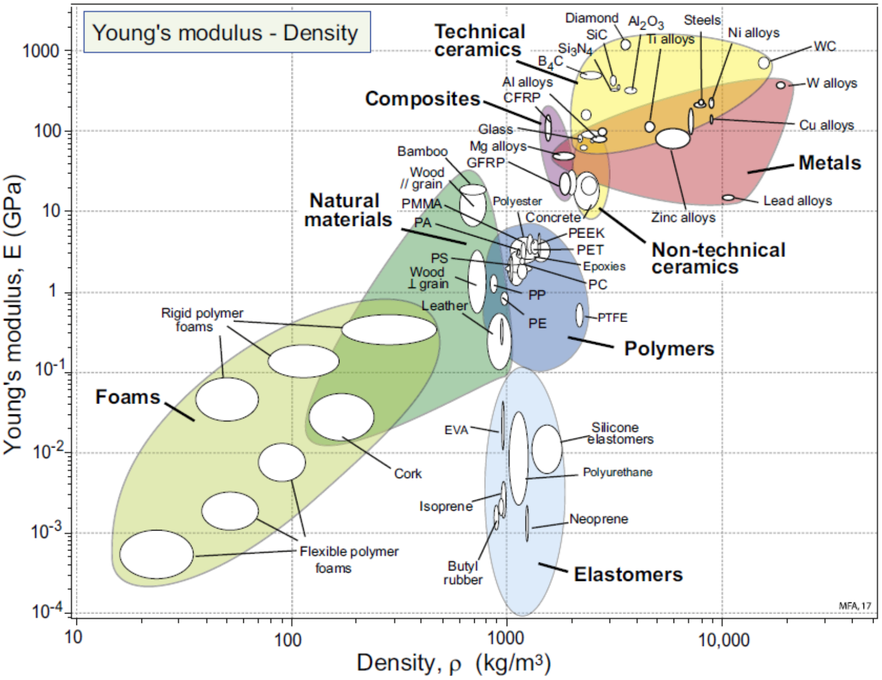

Figure 4.8 The Young's modulus–density chart.

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[7] Very-low density foams and gels (which can be thought of as molecular-scale, fluid-filled foams) can have lower moduli than this. As an example, gelatine (as in Jell-O) has a modulus of about 10^{-5} GPa.

This property chart gives an overview, showing where families and their members lie in $E-\rho$ space. We will use it in Chapter 5 to select materials for stiffness-limited applications in which weight must be minimised.

Anisotropy Glasses have disordered structures with properties that are *isotropic*, meaning they are the same no matter in which direction they are measured. Crystals, by contrast, are ordered, and because of this, their properties depend on the direction in which they are measured – they are *anisotropic*. Most real metals and ceramics are *polycrystalline*, made up of many tiny, randomly oriented crystals. This averages out the directionality in properties, so the aggregate behaves as if it were isotropic. Sometimes, though, anisotropy is important. Single crystals, drawn polymers and natural materials like wood are *anisotropic*; their properties depend on the direction in the material in which they are measured. Figure 4.8 has separate property bubbles for woods in each of the two loading directions, parallel and perpendicular to the grain. Fibre composites are yet more extreme: the modulus parallel to the fibres can be larger by a factor of 20 than that perpendicular to them – we explore why in the next section. Anisotropy must therefore be considered when wood and composite materials are selected.

4.8 Interatomic bonding and properties: the origin of elastic modulus

Recall from Section 4.6 the cohesive energy, H_c, is the energy per mol required to separate the atoms of a solid completely, giving neutral atoms at infinity (Figure 4.38). The greater the cohesive energy, the stronger are the bonds between the atoms. Materials with strong bonds have high melting points and high elastic moduli. Figure 4.39 shows the correlation between absolute melting temperature, T_m (here multiplied by the gas constant, R), and cohesive energy, H_c. The relationship is linear; the thermal energy RT_m at the melting point is about 3% of the cohesive energy.

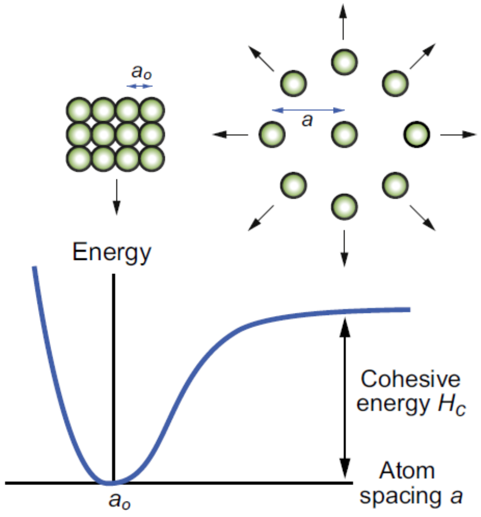


Figure 4.38 Cohesive energy.

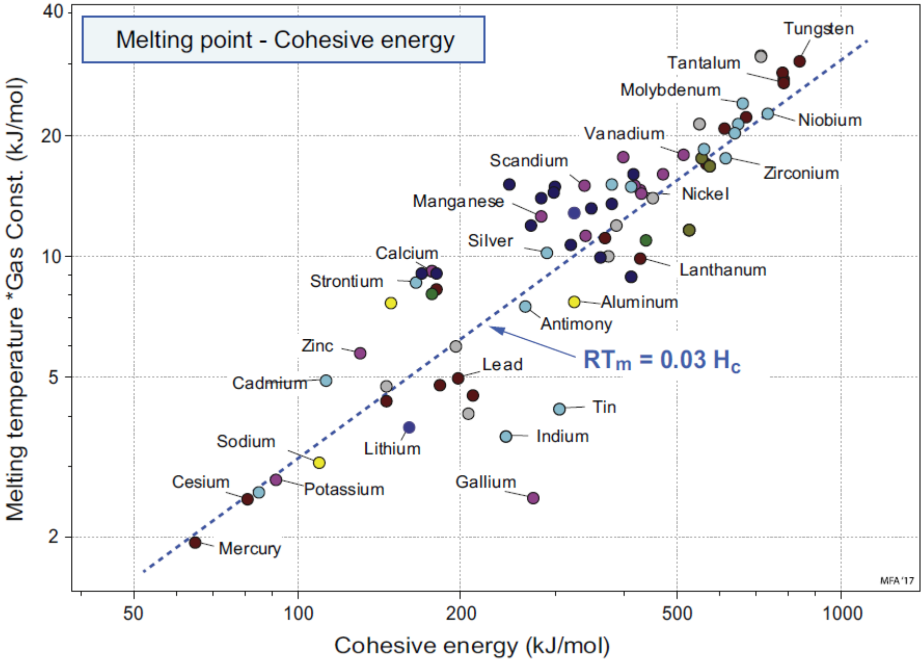


Figure 4.39 Melting temperature and cohesive energy of the elements.

The resistance of an elastic solid to 3D expansion like that sketched in Figure 4.38 is characterised by the *bulk modulus* K. Consider the work done if the volume occupied by one atom, V_o, is expanded by a volume ΔV – this is $K\Delta V/V_o$ (per unit volume). Let the critical expansion be $\Delta V^* = V_o/C^*$, at which point the bonds break, absorbing the cohesive energy, H_c; then if the molar volume is V_m:

$$K\frac{\Delta V^*}{V_o} = \frac{K}{C^*} = \frac{H_c}{V_m} \quad \text{or} \quad KV_m = C^* H_c \tag{4.24}$$

Figure 4.40 is a plot of KV_m against H_c for the elements, showing that this approximate linear relationship holds. The critical expansion constant $C^* \approx 3.5$, implying that a volume expansion of 1/3.5, or 30% (equivalent to a linear bond stretch of 10%), is enough to break the bond completely.

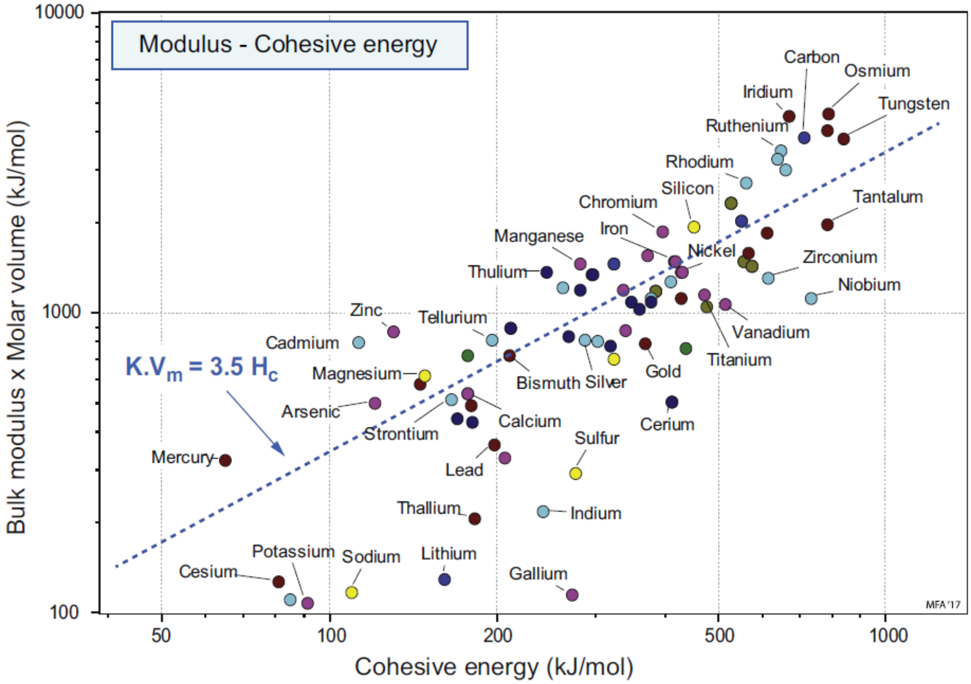


Figure 4.40 Bulk modulus and cohesive energy of the elements.

Bond stiffness and elastic moduli Think of atomic bonds as little springs linking the atom centres. Figure 4.41 shows the springs and the way the energy stored in them changes as the atoms are pulled apart or pushed together – it is an enlargement of the energy minimum in Figure 4.38. When no force is applied, the atoms have equilibrium spacing a_o; a force F pulls them apart a little, to $a_o + \delta$. A spring that stretches by δ under a force F has a stiffness, S, of:

$$S = \frac{F}{\delta} \tag{4.25}$$

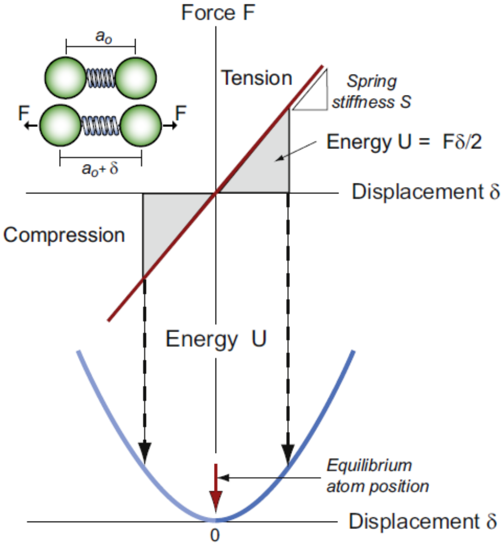


Figure 4.41 Bond stretching.

A force F applied to an atom of diameter a_o corresponds to a stress $\sigma = F/a_o^2$ assuming each atom occupies a cube of side a_o. A stretch of δ between two atoms separated by a distance a_o corresponds to a strain $\varepsilon = \delta/a_o$. Substituting these into equation (4.25) gives

$$\sigma = \frac{S}{a_o}\varepsilon = E\varepsilon$$

from which

$$E = \frac{S}{a_o} \tag{4.26}$$

Table 4.1 lists the stiffness of the different bond types and corresponding ranges for Young's modulus, E. The covalent bond is particularly stiff; diamond has a very high modulus because the carbon atom is small (giving a high bond density), and its atoms are linked by very stiff springs ($S = 200$ N/m). For most engineering metals, the metallic bond is somewhat less stiff ($S = 8-60$ N/m). But metals are close-packed, or nearly so, giving them high moduli – though not as high as that of diamond. Alloys contain a mixture of metallic bonding, between similar and dissimilar atoms, but these are of comparable stiffness. So when two elements are mixed, the modulus generally lies between those of the pure metals. Ionic bonds, found in many ceramics, have stiffnesses comparable with those of metals, giving them high moduli too.

Table 4.1 Bond energies, stiffnesses and moduli

Bond type	Example	Cohesive energy H_c (kJ/mol)	Bond stiffness S (N/m)	Young's modulus E (GPa)
Covalent	Carbon–carbon bond	100–1200	20–200	100–1000
Metallic	Engineering metals	60–850	8–60	20–400
Ionic	Sodium chloride	600–1600	4–100	30–400
Dipolar	Polyethylene	7–50	0.5–5	0.5–5

As noted earlier, the stiffness of a single crystal metal or ceramic will vary with direction relative to the atomic packing – they are *anisotropic* at the crystal scale. Most solids are *polycrystalline*, containing very many *grains* stuck together, each with their own lattice orientation (we return to this in Chapter 6). This averages out the directionality in the crystal stiffness, giving *isotropic* elastic moduli.

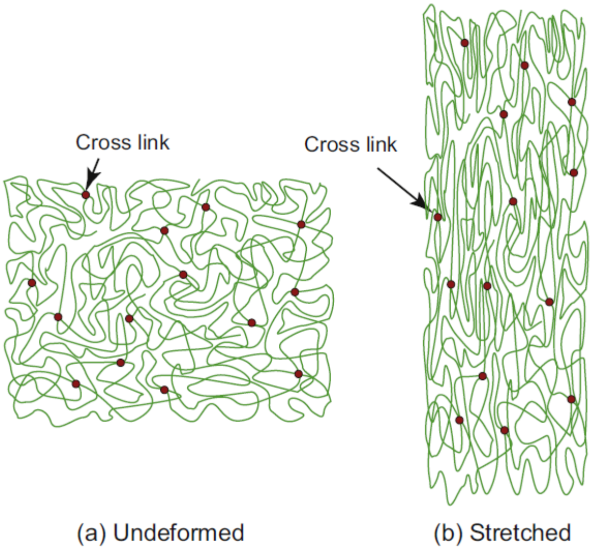
Polymers contain both strong covalent bonds along the polymer chain and weak hydrogen or van der Waals bonds ($S = 0.5$–5 N/m) between the chains; it is the weak bonds that stretch when the polymer is deformed, giving them low moduli. The random molecular structure is automatically isotropic. However, if the polymer is heavily drawn, the molecules align enough for the covalent bonds to be stretched, giving a much higher modulus (see the right-hand end of the polymer stress–strain curve of Figure 4.4). This is exploited in the production of polymer fibres, giving properties that are anisotropic and far superior along the fibre compared to a bulk polymer. This is discussed further in Chapter 19.

Table 4.1 allows an estimate to be made of the lower limit for Young's modulus for a true solid. The largest atoms ($a_o = 4 \times 10^{-10}$ m) bonded with the weakest bonds ($S = 0.5$ N/m) will have a modulus of roughly

$$E = \frac{0.5}{4 \times 10^{-10}} \approx 1 \text{ GPa} \tag{4.27}$$

Many polymers do have moduli of about this value. But as the E/ρ chart (Figure 4.8) shows, materials exist that have moduli that are much lower than this limit. They are either *foams* or *elastomers*. As we have seen, foams have low moduli because the cell walls bend easily when the material is loaded (Section 4.4). The origin of the moduli of elastomers takes a little more explaining.

The elastic moduli of elastomers An elastomer is a tangle of long-chain molecules with occasional cross-links, as in Figure 4.42(a). The bonds between the molecules, apart from the cross-links, are weak – so weak that, at room temperature, they have melted, meaning that segments are free to slide over each other. Were it not for the cross-links, the material would have no stiffness at all; it would be a viscous liquid.



(a) Undeformed (b) Stretched

Figure 4.42 Elastomer extension induces order, reducing entropy. Thermal energy tends to restore it.

The tangled structure of Figure 4.42(a) has high randomness, or as expressed in the language of thermodynamics, its entropy is high. Stretching it, as in Figure 4.42(b), aligns the molecules: some parts of it now begin to resemble the crystallites of Figure 4.37(b). Crystals are ordered; their entropy is low. Thermal energy displaces atoms, tending to increase entropy again. So here there is a resistance to stretching — a stiffness — that has nothing to do with bond stretching but with thermal pushback to strain-induced molecular ordering. The cross-links give the elastomer a 'memory' of the disordered shape it had to start with, allowing large strains that are elastic and fully recoverable. A full theory is complicated — it involves the statistical mechanics of long-chain tangles — so it is not easy to estimate the value of the modulus. The main thing to know is that the modulus of an elastomer is low because it has this strange thermodynamic origin, and (as a side effect) the modulus increases with temperature (unlike that of all other solids) because it is thermal pushback that is providing the stiffness.

Temperature dependence of polymer moduli: the glass transition temperature Crystalline solids have well-defined, sharp melting points. Amorphous polymers behave in a different way — bonding is weaker and more diffuse, with the inter-chain bonding spread over a spectrum of atomic spacing because of the tangled molecular structure. The amorphous regions gradually change properties from solid to liquid over a range centred on the *glass transition temperature*, T_g, as the weak inter-chain bonds progressively melt on heating. In semi-crystalline thermoplastics, however, the crystallites have their own sharp melting temperature, typically about $1.5 \times T_g$, due to the closer, regular packing of the chains. Elastomers and thermosets have a glass transition but do not melt on heating — because of the cross-linking, they degrade and burn instead.

How does the glass transition affect the Young's modulus? The answer is dependent on the type of polymer, since even if the weak bonding has gone, there can still be elastic behaviour above T_g. Figure 4.43 shows schematics of the variation of modulus with temperature. Below T_g, polymers are referred to as glassy, with the modulus controlled by the hydrogen bonding. Above T_g, amorphous thermoplastics (left-hand figure), show a tiny residual elasticity that stems from entanglements in the molecular structure, blurring into viscous flow. Semi-crystalline thermoplastics also show a drop in modulus across their glass transition, of the order of 10 times if the crystallinity is high, to a broad plateau in modulus where the response is referred to, somewhat misleadingly, as 'rubbery'. The degree of crystallinity determines how stiff the material remains above T_g, but eventually all thermoplastics melt and flow. Note the position of room temperature (RT) relative to T_g – in amorphous thermoplastics, T_g effectively sets the upper limit of usefulness of the polymer; in semi-crystalline, it sets the lower limit (due to their brittleness in the glassy state). Cross-linked behaviour is shown in Figure 4.43(b). Elastomers display a dramatic drop in modulus through T_g, by a factor of order 1000; the very low modulus of rubbers reflects the fact that at room temperature the material is already above T_g. The effect is well illustrated by immersing a rubber tube in liquid nitrogen, when it becomes stiff and brittle! Thermosets have a much higher degree of cross-linking, retaining a higher modulus as temperature falls, with heavily cross-linked thermosets barely showing a glass transition effect at all.

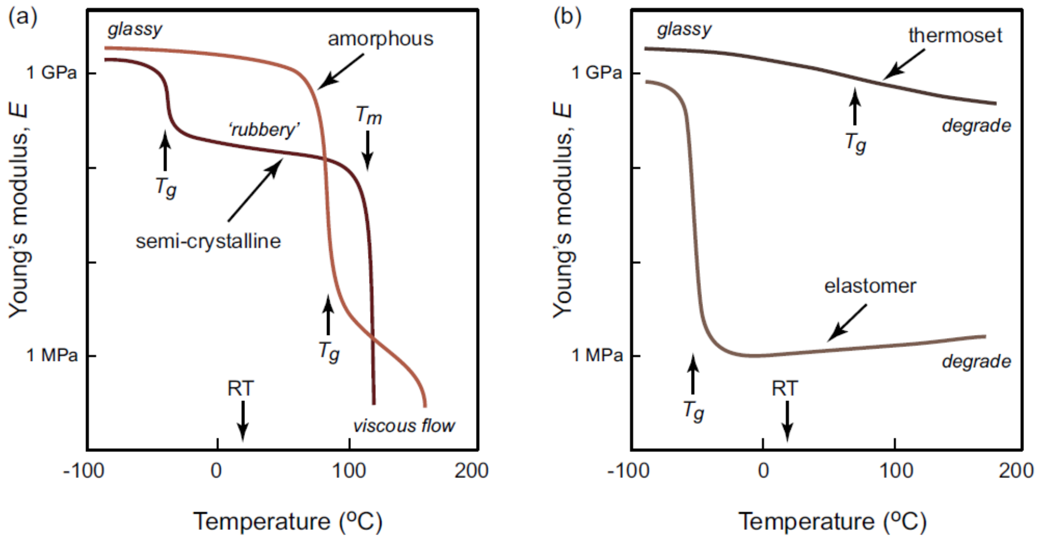


Figure 4.43 Schematic temperature dependence of Young's modulus for: (a) thermoplastics (amorphous and semi-crystalline); (b) elastomers and thermosets. The glass transition temperature T_g is where the weak inter-chain bonding is lost. RT indicates room temperature.

Polymer deformation shows other unusual characteristics. Since stretching the material is accompanied by some sliding of the molecules past one another, the stiffness is particularly sensitive to the rate of loading. Rapid loading does not give time for chain sliding; slow loading enables it, giving a quite different response. The glass transition temperature is therefore sensitive to the deformation rate. So at the same temperature, a polymer can switch from being floppy and resistant to fracture, to being much stiffer and glass-like, by pulling on it rapidly. Design to cope with the effect of temperature on polymers is discussed further in Chapter 13.

4.9 Summary and conclusions

When a solid is loaded, it initially deforms elastically. 'Elastic' means that when the load is removed, the solid springs back to its original shape. The material property that measures stiffness is the elastic modulus. We need three of them to deal with the different ways in which solids can be loaded:

- *Young's modulus*, E, measuring resistance to stretching and compressing;
- *shear modulus*, G, measuring resistance to twisting; and
- *bulk modulus*, K, measuring resistance to hydrostatic compression.

Many applications require stiffness at low weight, particularly ground, air and space vehicles, and that means a high modulus E and a low density ρ. The E-ρ property chart helps visualise this information and relate it to material classes.

The moduli have their origins in the stiffness of the bonds between atoms in a solid and in the packing of the atoms and thus the number of bonds per unit area. The atomic packing does not vary much from one solid to another, so the moduli mainly reflect the stiffness of the bonds. Bonding can take several forms, depending on how the electrons of the atoms interact. Metallic, covalent and ionic bonds are stiff; dipolar bonds are much less so, which is why steel has high moduli and PE has low. Bonding can be understood in terms of the electronegativity of atoms: their propensity to capture one or more electrons to become negative ions. A large difference in electronegativity between two elements favours ionic bonding; a small difference or no difference at all favours covalent bonding.

The density of a material is the weight of its atoms divided by the volume they occupy. Atoms do not differ much in size and packing, but they differ a great deal in weight. Thus the density is principally set by the atomic weight; as a general trend, the further down the periodic table we go, the greater the density.

There is very little that can be done to change the bond stiffness or atomic weight and packing of a solid, so at first sight, we are stuck with the moduli and densities of the materials we already have. But there are two ways to manipulate them: by mixing two materials to make composites, or by mixing a material with space to make foams. Both are powerful ways of creating 'new' materials that occupy regions of the $E-\rho$ map that were previously empty.