A very brief explanation of these phenomena is suggested by Fig. 5.9, namely that many polymers are essentially composites of hard crystalline regions embedded in a much softer amorphous matrix. (Some polymers are entirely amorphous). The amorphous part reacts to an applied stress more readily, to the extent it can, but it takes time to do so. We will examine this theme further in the next section.

5.5 Atomic Models of Mechanical Behavior

In this section we will explore how much of the mechanical behavior of materials we can interpret using our knowledge of the structure and interatomic forces in solids. We will focus on elastic and inelastic deformation of crystalline solids, in particular metals, but will outline the extension of these arguments to ceramics as well. At the end of this section, we will comment briefly on atomic processes in polymers. As always, these will be rather different than for crystalline materials.

5.5.1 Elastic Deformation: Mainly Metals

The principal definition of elastic deformation is that it must be recovered fully when the applied stress is removed. As a secondary characteristic we noted that elastic deformation usually, but not always, goes along with a linear relationship between the applied stress σ and the resulting strain ϵ.

For deformation to be elastic, it seems evident that it must involve atom-atom bonds that are only stretched but not broken. If breaking of bonds occurred on a large scale, there would be no reason to expect that all the broken bonds would be reformed as in the original state once the load is removed.

Fig. 5.14 illustrates this situation with a schematic drawing of a crystalline rod subject to a tensile stress. Clearly, the forces between neighboring atoms resist the deformation and will restore the original shape when the load is removed.

Although this picture appears to be qualitatively reasonable, it is worth asking whether it is in agreement with the notions put forth in Chapter 2 on atom-atom bonding in solids (see Figs. 2.8-2.10). For the sake of this discussion I have redrawn Fig. 2.8 as the new Fig. 5.15 below.

This time we are using $U(r)$ for the potential energy because E is the elastic modulus. $U_0 = U(r = r_0)$ is a measure of the interatomic bond energy and r_0 represents the equilibrium atom-atom separation. You also recall that $F(r) = \frac{dU}{dr}$ is the force on an atom, and the slope of $F(r)$ at r_0 is correlated with the stiffness, or what we now call the elastic modulus. Moreover, the slope of $F(r)$ at r_0 is essentially the curvature of the $U(r)$ curve at the minimum.

When you examine the properties of metals across the periodic table, you will make the interesting observation that the equilibrium distances r_0 (or equivalently the lattice constants a) vary by less than a factor 1.2. In fact, for the

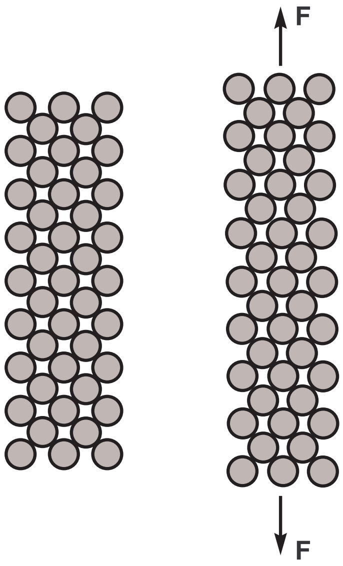

Figure 5.14: Atomic model of elastic deformation. Crystalline rod of FCC metal subject to load F in z-direction. Note axial stretching and lateral contraction.

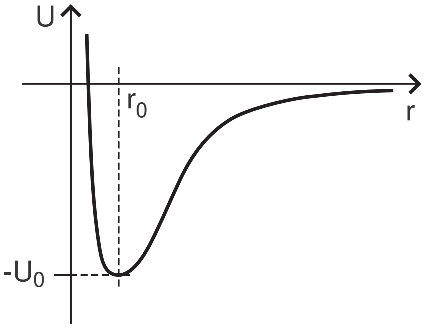

Figure 5.15: Potential energy $U(r)$ as a function of interatomic distance r.

common cubic metals, it would be an excellent approximation to say that $a = 0.35 \pm 0.06$ nm. So if you plotted $U(r)$ curves for different metals on the same graph, they would lie practically on top of each other and vary mostly with respect to their depth rather than their width or their position of r_0.

These observations suggest that the elastic modulus of a metal should be correlated with the depth U_0 of the $U(r)$ curve. Now, what experimental quantity should be used for U_0? Remember that $U(r)$ is a short-hand description of what really goes in a solid. $U(r)$ in a sense represents the interactions between a certain given atom and all its neighbors as if it were just between two atoms. Therefore, let us choose the so-called heat of atomization ΔH_a as the measure of U_0. ΔH_a is a thermodynamic quantity and designates the energy per atom it takes to atomize the solid, i.e. to separate all the atoms completely.

In Fig. 5.16, the elastic moduli of a number of metals are plotted as a function

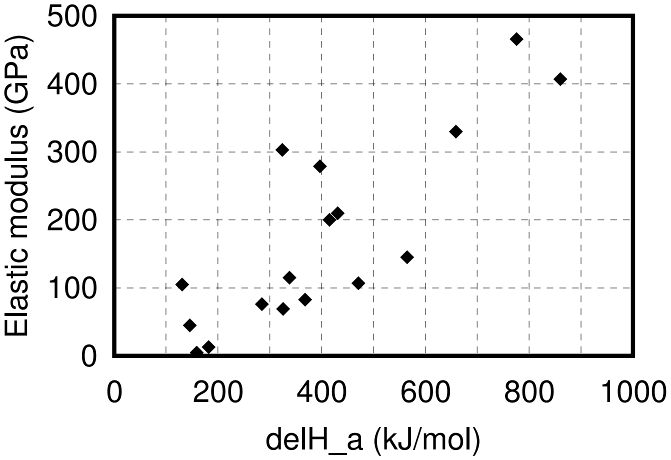

Figure 5.16: Plot of elastic modulus E versus heat of atomization ΔH_a for a sample of mostly common metals.

of the heat of atomization ΔH_a. Being thermodynamic quantities, the values for ΔH_a are listed per mole. The metals used for the plot are, in order of increasing E (from 5 to 466 GPa): Li, Ba, Mg, Al, Ag, Au, Zn, Ti, Cu, Pt, Fe, Ni, Cr, Be, Mo, W , Re. This list should represent a good sample, as it contains about equal numbers of BCC, FCC, and HCP metals. You will agree that the plot shows a clear correlation between E and ΔH_a, although there is also a fair amount of scatter between the data points.

An even better correlation exists between the melting temperature T_m and ΔH_a, as you can see in Fig. 5.17. Even though in the molten state atoms are not separated much farther than in the crystalline solid state, the quantity ΔH_a, as an average atom-atom bonding energy, is apparently an excellent predictor of T_m. It follows from these two plots that a very good correlation also exists between T_m and E.

An explicit function with the general form of $U(r)$ in Fig. 5.15 is often used to model the interactions between atoms in a solid in general, i.e. between a specific atom and *all* its neighbors. The function is known as the Lennard-Jones potential. Applied to our situation, it can be written as

$$U(r) = U_0\,[\,(\frac{r_0}{r})^{12} - 2\,(\frac{r_0}{r})^{6}\,] \tag{5.20}$$

You can easily convince yourself that it has a minimum of $-U_0$ at $r = r_0$ by taking the first derivative. The attractive part is negative and there is some physical justification for it having the form r^{-6}, but the r^{-12} term is just a mathematically convenient form for the steep repulsive part.

Fig. 5.18 displays the Lennard-Jones potential in a reduced form, $u(x)$, to-

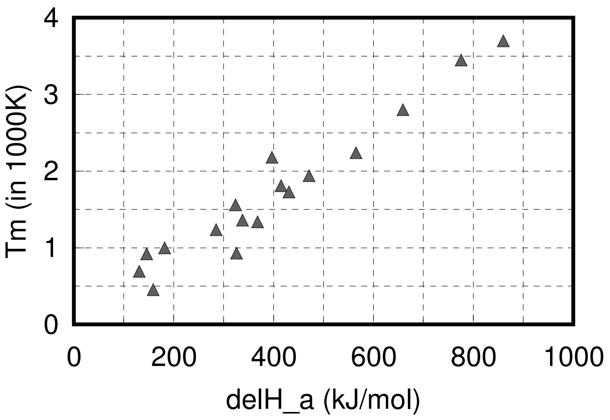

Figure 5.17: Plot of melting temperature T_m versus heat of atomization ΔH_a for the same metals as in Fig. 5.16.

gether with the associated reduced force $f(x)$, by letting $U_0 = 1$ and $x = r/r_0$. That is, the equations plotted are:

$$u(x) = \frac{1}{x^{12}} - \frac{2}{x^6} \tag{5.21}$$

$$f(x) = \frac{du}{dx} = -\frac{12}{x^{13}} + \frac{12}{x^7} \tag{5.22}$$

The main thing you should take away from this graph is that the potential is very steep indeed in its repulsive part, and that on the attractive side it quickly approaches the value 0. You can also see that $U(r)$ is clearly asymmetric near its minimum.

If we accept this potential energy function as reasonable, then it is straightforward to derive a mathematical expression for the elastic modulus from it.

Have another look at Fig. 5.14: Assume that at the ends where the force F is applied, the cross-sectional area per atom is A_a. Now, let the force per atom F_a be given by the derivative of $U(r)$ in Eq. 5.20. Then by the definition of F_a, Hooke's Law can be written as:

$$\sigma = \frac{F_a}{A_a} = \frac{\frac{dU}{dr}}{A_a} = E\,\frac{\Delta r}{r_0} \tag{5.23}$$

Think of $\frac{\Delta r}{r_0}$ as the strain of an atom-atom bond and Eq. 5.23 as Hooke's Law for an atom-atom bond.

From here it is just a matter of taking the derivative of Eq. 5.20 twice and doing some algebra to arrive at an expression for the *macroscopic* quantity E in terms of *atomic* parameters. First, solve Eq. 5.23 for E:

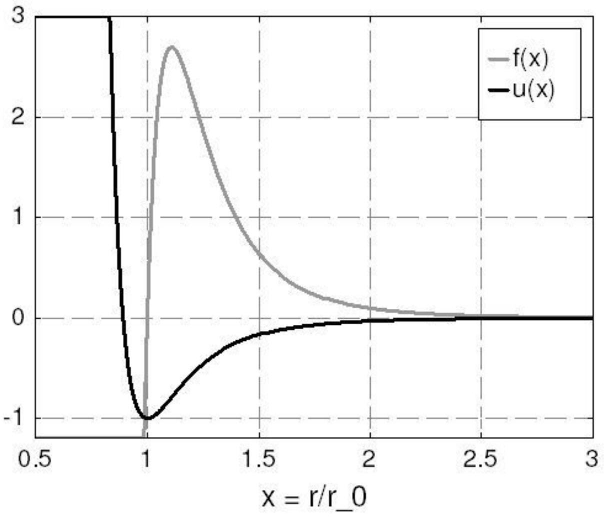

Figure 5.18: Plots of Lennard-Jones potential energy (black curve) and associated atom-atom force (light gray curve).

$$E = \frac{1}{A_a}\,\frac{F_a}{\frac{\Delta r}{r_0}} = \frac{r_0}{A_a}\,\frac{dF_a}{dr}\bigg|_{r=r_0} \tag{5.24}$$

This can be evaluated explicitly using $\frac{dF_a}{dr} = \frac{d^2U}{dr^2}$, with the result

$$E = 72\,\frac{U_0}{r_0\,A_a} \tag{5.25}$$

At the simplest level, Eq. 5.25 says that the elastic modulus E should be proportional to the atom-atom bond energy U_0. This is, of course, exactly what the data demonstrated in Fig. 5.16 above. To what extent Eq. 5.25 is quantitatively accurate will be explored in the homework.

5.5.2 Plastic Deformation in Metals

Whereas in the previous section it appeared that our simple atomic solid model gave a reasonable description of elastic deformation, it may likely be a different matter with inelastic, or plastic, deformation. Remember: The latter involves large-scale, permanent deformation with the breaking and remaking of atom-atom bonds, not just the stretching of them.

Moreover, when you revisit Fig. 5.14, it is hard to see how, under the influence of a tensile stress, bonds can be broken and then quickly reformed. It