is a representative value for the "melting point" of a glass. The point $\eta = 10^{12}$ Pa s is sometimes also referred to as the annealing point, because at that point internal stresses in the material are relieved on a time scale of minutes. The working range denotes the range of conditions typically used in glass-forming processes. At temperatures above the strain point, a glass is rigid enough so that it can be handled easily without introducing new stresses.

7.5.3   Solidification: Amorphous Solids

We begin our discussion of solidification as the reverse of melting by considering amorphous materials. This is by far the simpler situation. As I emphasized above, with respect to detailed structure, there is very little difference between a molten glass at high temperature and its solid, rigid form at much lower temperature. However, one minor structural difference is evident from the plot of specific volume vs. T in Fig. 7.6: The solid glass has a higher density than the molten glass.

Keep in mind that the curve for specific volume vs. T in Fig. 7.6 is in principle reversible: It applies for going up as well as going down in temperature. But in the process of cooling a new effect comes into play. Even though what happens during cooling is mainly that the building blocks of the glass loose mobility, how closely packed they end up depends on how rapidly you cool. The SiO_4 tetrahedra, or the polymer chains, try to achieve the lowest energy configuration possible, but this requires time! Therefore, as the glass becomes rigid, the final configuration is the more densely packed the slower the cooling rate. This is why the $\rho(T)^{-1}$ curve in Fig. 7.6 shows two branches below T_g, an upper one for a higher cooling rate and a lower one for a slower cooling rate. In this light, it becomes clear why T_g is not an exact number: T_g depends on the cooling rate.

7.5.4   Solidification: Crystalline Solids

Forming a crystalline solid from the melt upon cooling is a much more complex process than simply freezing in the disordered structure of a glass. In a crystal, the structure with the lowest energy has long-range order. Achieving this highly ordered state requires coordinated motion of a large number of building blocks, atoms or molecules, to align themselves precisely with each other.

When you think of metals, you may conclude that it is almost impossible not to end up with a crystalline, or at least polycrystalline, material. When you think of SiO_2 or ionic materials, you realize that it could go either way. For the case of polymers, forming crystals may be the exception, or it may not be possible at all! So, what does it take for a material to solidify as a crystal, rather than as an amorphous solid?

The answer is that time, i.e. the cooling time, is again a factor in many systems, in that the atoms or molecules need enough time to be able to find their

preferred crystal positions. But, most importantly, the formation of a crystalline phase, i.e. a large crystal, is greatly facilitated if one starts out with a small crystal! This requires some explaining.

First, with regard to the relevant time scale, this depends on the type of material in question. As you recall, metals are characterized by a strong non-directional interaction which is the same between any atoms. It turns out that near the melting point, the mobility of metal atoms is large enough so that the time scale on which atoms are able to find their preferred crystal positions is generally much smaller than the time scale on which cooling takes place. This is certainly true for processes relevant in engineering practice, although it has been possible to create small amounts of amorphous metals in the laboratory, under conditions of extremely rapid cooling (rapid meaning a cooling rate of something like $10^6 \, \mathrm{Ks^{-1}}$, depending on the composition of the metal).

For an ionic solid, the time scale to allow for crystallization is longer, because of the additional constraints due to the different ionic sizes and the conditions of electrostatic repulsion/attraction between like/unlike ions. For polymers to form crystals, the time scale is longer yet due to the constraints imposed by the geometry of the chain molecules.

Second, the formation of a crystal is really envisioned to involve two linked processes:

1) ***formation of a crystalline nucleus***,   followed by

2) ***further growth*** of the initial nucleus.

In order for atoms to know where they are supposed to go, namely into a regular array of lattice sites, one should start out with a small template which already has the required order and symmetry. Then, adding more atoms in the right places is simply a matter of letting them find the lowest energy positions proscribed by the template.

So, forming a crystalline solid amounts to maintaining conditions which allow for crystal templates, so-called nuclei, to form in the disordered liquid and, at the same time, for nuclei to keep growing to sizes of many thousands of atom-atom distances. In short, forming a crystalline solid involves **nucleation** followed by **growth** of crystallites.

As we will explain shortly, nucleation and growth are in a sense competing processes. Conditions may be such that nucleation occurs readily, but growth is impeded greatly. On the other hand, conditions may be suitable for growth yet not enough nuclei are being formed. In either case, the formation of a crystalline phase would not be favored. If the conditions are such that they do lead to formation of a crystalline phase, then it is clear that how the competition between nucleation and growth plays out in practice will have a great deal of influence on the final microstructure of the solid phase.

Nucleation

Let us pause briefly to review the process we are trying to describe. We are interested in how a crystalline solid forms as we cool down a piece of molten material. For the sake of simplicity let us assume we are dealing with pure metal.

If during the cool-down we stopped exactly at the melting point T_m, nothing would happen because right at T_m liquid and solid would be in equilibrium if there were any solid, but no solid has formed yet. In order to provide a driving force for solidification, we have to create a condition called **undercooling**, i.e. we have to take T a little below T_m. Yet even under that condition, crystalline nuclei do not form automatically, and here is why:

completely disordered
liquid region

liquid region with
crystal nucleus
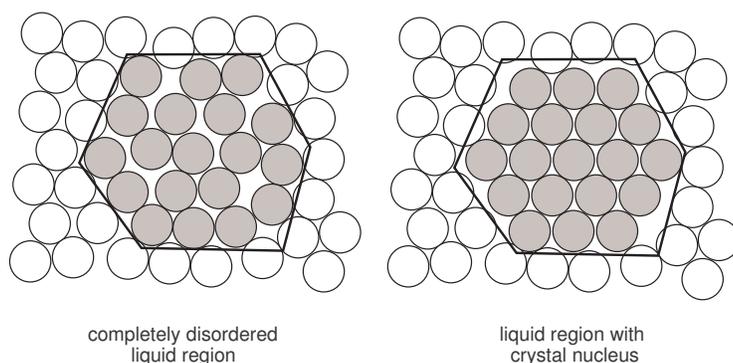
Figure 7.9: Schematic comparison of a completely disordered liquid and a liquid with a crystalline nucleus in it.

The panel on the left in Fig. 7.9 shows an entire region of disordered liquid. The gray atoms are singled out because they are the ones that will form a crystalline nucleus in the right panel. The white disordered atoms are in their original disordered configuration in both panels. The polygon is drawn to circumscribe an approximate boundary around the disordered gray atoms, and it is the same as well on both sides.

When you examine the ordered gray atoms in the panel on the right, you will realize that two things have happened to them compared to the liquid state. First, by forming a crystal they have lowered their energy: All else being the same, hexagonal close-packing is the most favored configuration. However, these atoms have also had to pull away a little from their still disordered neighbors around the periphery. This is perhaps most evident in the upper left-hand and lower right-hand corners of the polygon. This second effect basically amounts to creating a new surface for the crystal nucleus, thereby increasing the energy of the gray atoms.

Therefore, the fate of the transient crystal nucleus will depend on the bal-

ance between the two effects of lowering the "bulk" energy and raising the "surface" energy of the gray atoms. Most interestingly, as we will show next, there exists a critical size for a nucleus, in the sense that a nucleus smaller than the critical size will revert to a disordered state, but a nucleus larger than the critical size will continue to grow as a crystal.

Consider now a spherical crystal nucleus with radius r and its change in free energy ΔG relative to the liquid state. That is, ΔG is the difference between the free energy of the gray atoms of Fig. 7.9 aggregated into a nucleus and the disordered gray atoms. We argued above that ΔG has two parts, a bulk part due to the lowered energy of the ordered state, and a surface part due to the extra energy involved in creating a new surface for the nucleus.
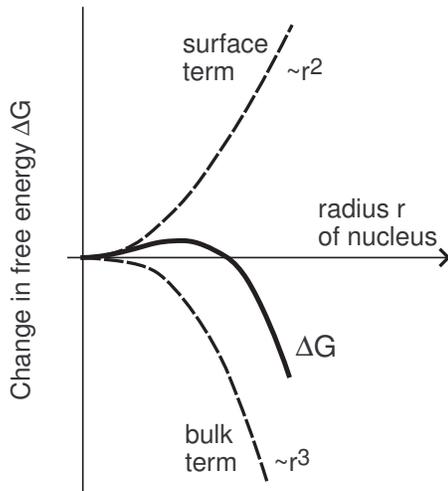
Figure 7.10:
Contributions to the change in free energy ΔG of a spherical nucleus. Note the bulk and surface parts, and their characteristic dependencies on the radius r of the nucleus.

What we can say immediately is that the bulk part must be proportional to the volume of the nucleus, and the surface part proportional to the surface area of the nucleus. Explicitly, assuming spherical nuclei with radius r:

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \qquad (7.7)$$

where ΔG_v is the bulk free energy difference per unit volume and γ is the surface free energy difference per unit area. Note that for $T < T_m$, as per our earlier argument, ΔG_v must be < 0.

Clearly, $\Delta G = 0$ at r = 0. Furthermore, because of these dependencies on r, it follows that for r very close to 0, the surface terms dominates, i.e. ΔG must increase initially. On the other hand, for large r the bulk term dominates, and thus ΔG must turn negative at large enough r. Therefore, ΔG *must have a maximum* as a function of r !