

Fundamentals of the Glassy State

2.1 What is Glass?

Our impressions of the nature of glass are affected by everyday experience with the material. To the layman, glass is a transparent solid that breaks easily. Yet a number of glass types, in particular the chalcogenides and metallic glasses, are opaque in the visible spectrum. Also, high-strength glasses can be made by a variety of techniques, some being used in bulletproof security glazing. The American Society for Testing Materials (ASTM) at one time defined glass as “*an inorganic product of fusion which has been cooled to a rigid condition without crystallizing.*” Even this definition is too restrictive, as many organic glass systems are known and fusion is not the only means of making a glass. The sol-gel process (see Section 20.3.3) of making a glass avoids the normally high temperatures employed for the fusion of glass. Chemical vapor deposition is yet another technique which completely avoids fusion of constituent materials.

The outward appearance of glasses is essentially solid-like. The density, the mechanical properties, and the thermal properties of glasses are similar to those of the corresponding crystals. However, unlike crystals, glasses do not have a sharp, well-defined melting point. Unlike most crystals, glasses do not cleave in preferred directions. In the absence of applied forces and internal stresses, glasses are essentially isotropic. The isotropy of physical

properties makes glasses resemble liquids. It follows that the atomic arrangements in glass must display the long-range disorder typical of liquids. In order not to be overly restrictive, we are left to *define glass as a "solid with liquid like structure," "a noncrystalline solid," or simply as "an amorphous solid,"* with the understanding that the amorphous characteristic here is intended to describe atomic disorder as evidenced by an x-ray diffraction (XRD) analysis; it excludes substances such as "amorphous" powders that may simply be "micro-crystals" and that display more or less sharp peaks in XRD analysis. Many physicists restrict the word "glass" to mean an amorphous solid that undergoes a "glass transition" when heated. Glass transition, which we shall discuss in detail in Chapter 13, involves a continuity of volume and a steep change in physical properties such as the specific heat, thermal expansion, etc., from a "supercooled" liquid state. Substances such as Si and Ge have been brought to the disordered solid state only by means of thin-film techniques (thermal evaporation, ion implantation, etc.) not involving melt-quenching. Apparently, this disordered state for both materials is thought to have a volume discontinuity from the liquid state. As a result, α -Si and α -Ge are often excluded from the class of substances called "glass" by the physicists. In our description of the word "glass" we will include these and other amorphous solids where the volume-temperature relationships are yet to be established. To get a clearer picture of the fundamentals of glass, the balance of this chapter is devoted to a consideration of the volume-temperature relationship (the V - T diagram) of the glass with respect to a liquid and a crystal, and pair correlation/radial distribution functions to describe atomic disorder in terms of the spatial relationships between the locations of various atoms in a substance.

2.2. The V - T Diagram

Consider a small volume of material at a high temperature in liquid form. Its state is given by the point "a" on the V - T diagram (Fig. 2-1). On cooling, the volume gradually decreases along the path "abc." Point "b" corresponds to T_m , the melting point of the corresponding crystal, which may be defined as the temperature at which the solid and the liquid have the same vapor pressure or have the same Gibbs free energy. At this temperature, an infinitely small amount of crystals is in thermodynamic equilibrium with the liquid. However, for a perceptible level of crystallization, some finite amount of undercooling of the liquid to a point "c" below T_m is required. Crystallization occurs if, and only if, (i) there are a sufficiently large number of nuclei present in the mass, and (ii) a large enough crystal growth rate exists. The location of the point "c" below T_m varies depending upon when the thermodynamic

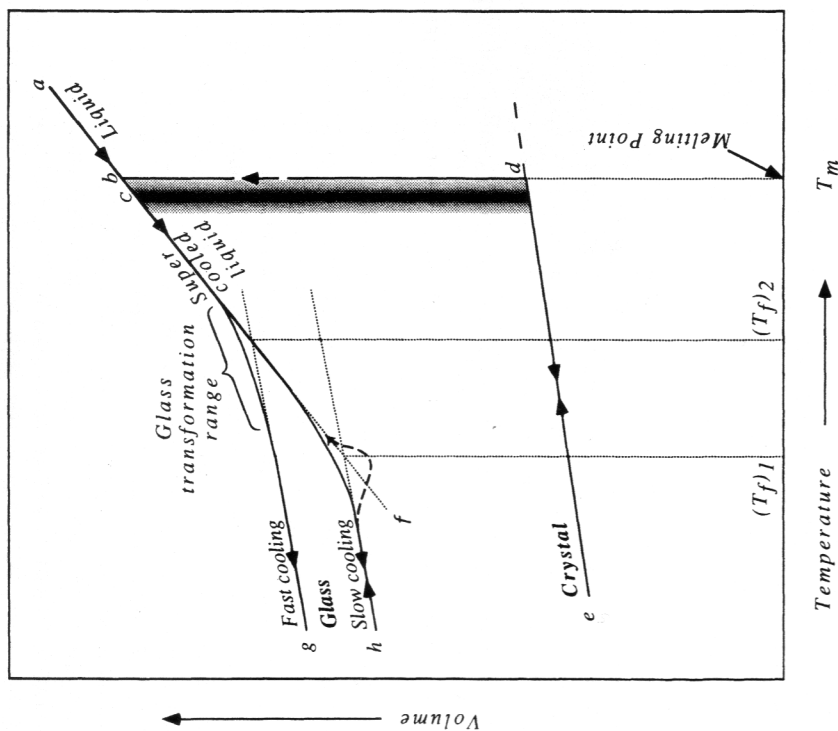


Figure 2-1. The volume-temperature diagram for a glass-forming liquid.

driving force created by the undercooling causes a particular group of atoms to transform from the liquid state to the crystal state, and upon the velocity at which the atoms from the liquid can be transported to the crystal-liquid interface. For these reasons, we have shown a wide, shaded region with varying probability representing the crystallization path. (These thermodynamic and kinetic concepts are explained further in Section 3.3.) A volume shrinkage generally accompanies the crystallization. Upon further cooling, the crystals so formed shrink along the crystal line to the point "e."

If crystallization does not occur below T_m (mostly because the cooling rate is high), the liquid mass moves into the **supercooled liquid** state along the line "bcf," which is an extrapolation of the line "abc." No discontinuities in the V - T are observed. The volume, however, shrinks continuously, i.e., the

produces atomic disorder in a substance and proceeds from the surface inwards. Hence, crystals may be superheated to temperatures beyond T_m if the heat is provided internally or if melting produces a very high-viscosity liquid phase such that atoms within the interior of the crystal do not have "room or time to disorder." Ordinarily, the melting of a crystal is much sharper (on the temperature scale) than the freezing of a liquid.

Note that, with regard to the slight separation "b-c" between the crystallization and the melting paths near T_m , the $V-T$ diagram presented here differs slightly from those usually presented by other authors.

To understand the structural relationship between the glassy state and other states of matter, we need to understand the pair distribution function and the radial distribution function used commonly to describe the distribution of atoms in amorphous solids.

2.3. Pair Correlation Function and Radial Distribution Function

In a material (gas, liquid, or solid) where the average number density of atoms is $\rho_0 = n/v$, n being the total number of atoms and v the total volume, the number density of atoms at a distance r from an origin atom is given by $\rho_0 g(r)$. The function $g(r)$ is the ratio of the number density of atoms at r to the homogeneous density, ρ_0 , and is called the **pair distribution function**. The term $\rho_0 g(r) dr$ then gives the probability, dp , of finding an atom center in dr that is at a distance r from the origin atom. (The reader should note that $g(r)$ is a probability density function.) In a disordered system the number density approaches ρ_0 at very large distances from any given origin atom, and hence

$$\lim_{r \rightarrow \infty} g(r) = 1.$$

The increasing repulsion between overlapping electron orbitals (Pauli's exclusion principle) discourages the close approach of two atoms, i.e.,

$$\lim_{r \rightarrow 0} g(r) = 0.$$

A schematic variation of $g(r)$ with r is sketched in Fig. 2-2a. Note that the function may rise from zero and oscillate about 1 until asymptotically approaching 1. The magnitude of the oscillations directly gives the higher or lower density at r .

Some authors define the **pair correlation function**, $h(r)$, by

$$h(r) = g(r) - 1.$$

structure of the liquid rearranges itself into a lower volume along the line "bcf" required by the lower energy corresponding to a lowered temperature. As cooling continues, the molecules become less and less mobile, i.e., the viscosity of the system rapidly increases. At sufficiently low temperatures, the molecular groups cannot rearrange themselves fast enough to reach the volume characteristic of that temperature. The state line then starts a smooth departure from "bcf" and soon becomes a near-straight line (often roughly parallel to "de"), ending at point "g," when cooled fast, or at "h," when cooled slowly. The material in the near-straight, low-temperature part of the curve behaves essentially as a solid. *This is the glassy state.*

The smooth curve between the onset of departure from the supercooled liquid line and the completion to a seemingly rigid condition is termed the **glass transition region**, or the **glass transformation range**. It must be emphasized that the transition to the glassy state does not occur at a single, sharp value of the temperature. In the upper regions, glass has a viscosity of $\sim 10^8$ Pa-s ($= 10^9$ poise) or less, whereas in the glassy state the viscosity exceeds $\sim 10^{15}$ Pa-s or more to qualify for appearance as a solid. The intersection of the extrapolated glass line and the supercooled liquid line is termed the **fictive temperature** (T_f). One may imagine that T_f is the temperature at which the structure of the supercooled liquid is instantly frozen into the glass. (It will be stated in Chapter 13, that this concept is only approximately correct.)

The departure from the supercooled liquid line is dependent upon the rate of cooling. Slower cooling allows the structure to rearrange itself to stay on "bcf" somewhat longer, and hence the more slowly cooled glass at "h" would be expected to have a lower volume (higher density) and a lower fictive temperature than a more quickly cooled glass at point "g." For now, it suffices to suggest that the volume of the corresponding crystal is expected to be less than that of the most slowly cooled glass. (There are some interesting anomalies and questions. Some are discussed here. Some others will be discussed in greater detail in Chapter 13.)

When the glass at "h" is reheated, the state smoothly moves through the transition region along the dashed curve to the supercooled liquid state "fcb" and ultimately to the liquid state. The $V-T$ curve *NEVER retraces its path in the transition region* (for reasons discussed in Chapter 13). Other than the gradually increasing fluidity and, perhaps, a color change due to radiative emission, in general there are no changes in the physical appearance of glass with the reheating.

If the crystals at "e" are heated, the state will move along the crystal line up to "d" (= the melting temperature, T_m) past the shaded region, melt at T_m to reach point "b," and subsequently follow the liquid path "ba." One may question whether it is possible to superheat a crystal or not. Melting

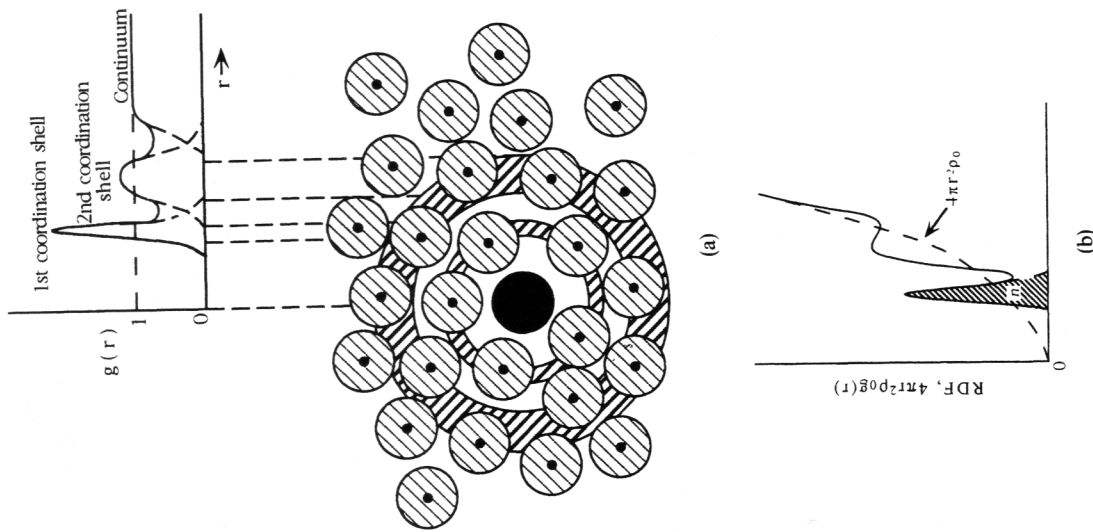


Figure 2-2. (a) Pair distribution function, $g(r)$, versus radial distance, r . (b) Radial distribution function versus r . For uniform probability, the RDF is simply a parabola.

This definition has the advantage that, in disordered systems, $h(r)$ approaches zero at large distances, implying no correlation (which agrees with our intuition), and approaches -1 at $r = 0$, implying perfect negative correlation corresponding to the non-overlap of the atoms (again agreeing with our intuition). Both the $g(r)$ and $h(r)$ provide essentially the same information.

Instead of the pair distribution function or the pair correlation function, sometimes the **radial distribution function** (the RDF) is also used. The RDF is defined by $4\pi r^2 \rho_0 g(r)$, which is the radial density of atoms at distance r from the origin atom A. The number of atoms in a spherical shell at a distance r and $r + dr$ from A is given by $4\pi r^2 \rho_0 g(r) dr$. Clearly, at large values of r , the RDF tends to become a smooth parabola (Fig. 2-2b). If the RDF is integrated between r_1 and r_2 , where the limits describe the lower and the upper end of a "peak," then by definition

$$\int_{r_1}^{r_2} 4\pi r^2 \rho_0 g(r) dr = \text{the area under the peak,}$$

[which is equal to the number of neighbors to the origin atom A residing within r_1 and r_2].

If the peak is the first one from origin, then the preceding expression gives the first coordination number for A (Fig. 2-2b). In polyatomic systems, it is usual to find atoms of a different type B around the origin atom A. The expression then gives the coordination number of B about A.

Occasionally the RDFs are plotted as $[4\pi r^2 \rho_0 g(r) - 4\pi r^2 \rho_0]$ versus r . In such a plot, the parabola has been subtracted out, and the distribution function oscillates about the abscissa. Other ways of plotting the data are the reduced RDF, sometimes called the total correlation function $t(r)$, defined by

$$t(r) = 4\pi r \rho_0 g(r),$$

and the differential correlation function $d(r)$, defined by

$$d(r) = [4\pi r \rho_0 g(r) - 4\pi r \rho_0].$$

(Note: The reader may find that various authors use different names for many of these distribution functions.)

It is easy to note that the reduced functions have simply been obtained by dividing $g(r)$ and the RDF by r . The division by r makes the peaks more symmetrical, and hence the peaks can be defined with more precision, allowing better integration of the area to determine the coordination numbers. Typical plots of the reduced functions are shown in Fig. 2-3.

The pair correlation function and the radial distribution function are important for the study of noncrystalline solids, not only because they describe the mutual relationship between the location of various atoms, but also because these can be experimentally measured after Fourier transformation of x-ray diffraction (XRD) or neutron or electron diffraction data. In diffraction experiments, the scattered intensity is recorded as a function of $Q = (4\pi \sin \theta)/\lambda$, where $\lambda =$ wavelength and θ is the scattering angle. After

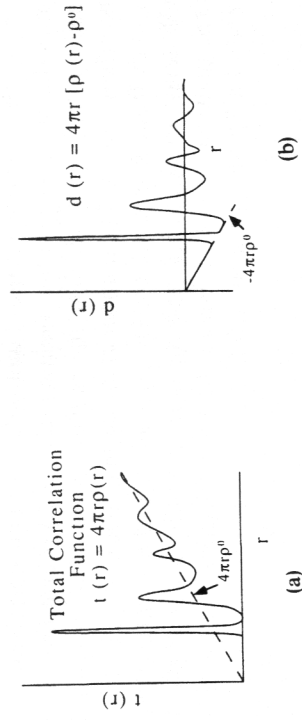


Figure 2-3. (a) Total correlation function. (b) Differential correlation function. correction and normalization, one obtains the coherent intensity $I_{coh}(Q)$ as a function of Q , from which the total structure factor $S(Q)$ is obtained. The Fourier transform of $S(Q)$ is simply the differential correlation function $d(r)$.

The simplified pair distribution functions of the various states of matter are shown in Fig. 2-4. Ideally, the crystals exhibit a regular, periodic array of atoms represented by vertical lines, but these lines broaden somewhat to become sharp peaks because of the presence of thermal vibrations about the equilibrium positions and defects. In gases, there is no equilibrium position: gas atoms impinge upon each other and "penetrate" into each other some distance until Pauli's exclusion principle stops further penetration. The function $g(r)$, for a snapshot in time, rapidly rises and becomes a uniform value irrespective of the distance from the origin atom. (For a hard sphere model, $g(r)$ would be a step function at the hard sphere diameter.) In liquids, the probability of finding atoms is neither regularly spaced as in crystals nor uniform as in gases. For the first few neighbors, definite peaks occur at locations bearing some resemblance to the locations found in crystals. Because of variations in the interatomic distances, the peaks get broader as the distance from the origin atom increases.

Because the glassy state is an extrapolation of the liquid state to lower temperatures, it is expected that glass has a liquidlike structure. This indeed is the case, as is shown in Fig. 2-5, where the PDF of various ion pairs is shown in both liquid and glassy 45CaO-55SiO₂ (mol. %). In liquids, the thermal vibrations (and subsequent time-averaging) broaden the peaks relative to the glasses, where the atomic motions are relatively frozen in space. Figure 2-6 shows a comparison of the experimentally measured x-ray diffraction (XRD) spectra of vitreous silica, cristobalite, and silica gel. Note that, unlike the sharp peaks in the crystal form, peaks in vitreous silica occur in the form of a broad hump. However, the hump is located roughly at the

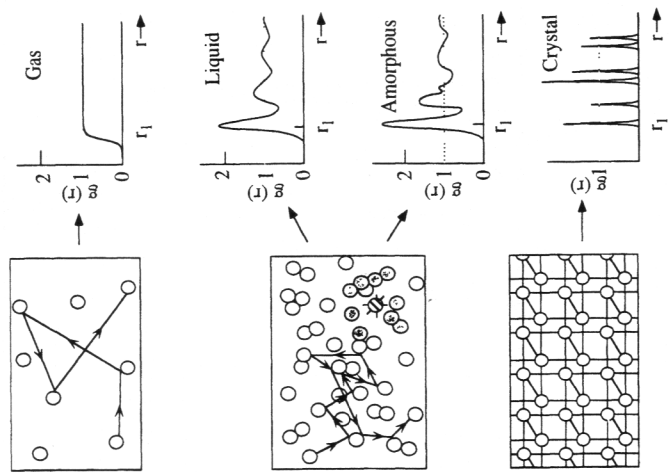


Figure 2-4. Schematic diagram of the atomic and pair distribution function for gas, liquid, amorphous, and crystal states. In gases, because of the kinetic energy, the atoms "penetrate" into each other slightly more deeper than in the condensed state. (Modified and redrawn from Y. Wasada, *Metal Phys. Seminar* 1, 305 (1976).)

same place as the primary peak in cristobalite. In essence, in both the liquids and the glasses, there may be some short-range order; however, the long-range order typical of crystalline arrangement is absent. The similarity of the broad hump to that observed in silica gel led Randall *et al.* [1] to conclude that glass consisted of an aggregate of finely divided crystals (perhaps finer than in a gel). They stated that "the difference between a crystalline state, on the one hand, and the 'vitreous' and 'amorphous' on the other is one of degree, not of kind." However, the small-angle scattering typically seen in the gel spectra is nearly absent in the glass spectra. This observation led Warren [2] to suggest that the crystal size in the glass would have to be of the order of a few angstroms, hardly bigger than a single unit cell, at which point the concept of a crystal becomes meaningless. The $V-T$ diagram illustrates the fact that there are no direct paths between a crystalline state and a glassy state using heat as a means for change. From either state, one must approach

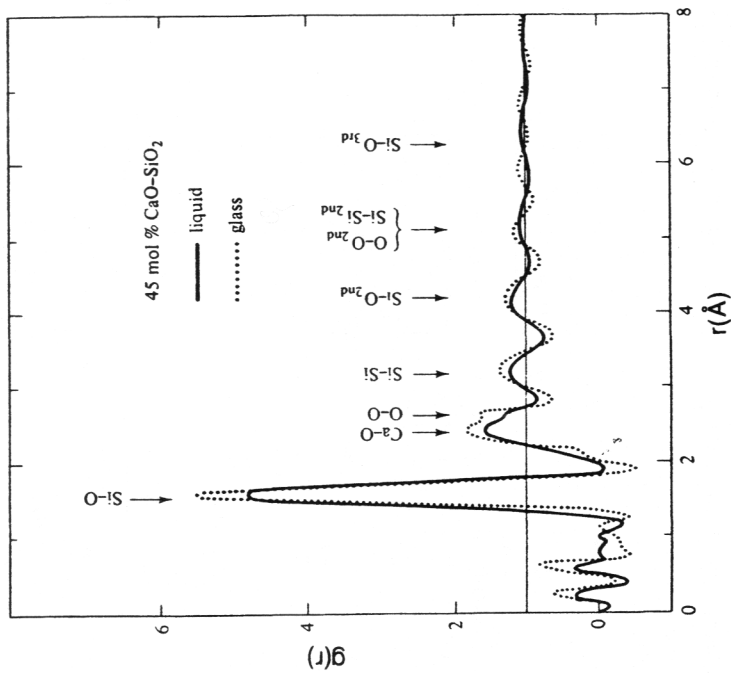


Figure 2-5. Comparison of $g(r)$ between the glassy and the liquid states for $45\text{CaO}-55\text{SiO}_2$. (After Y. Waseda and J. M. Toguri, *Met. Trans.* **8B**, 563 (1977).)

at least the supercooled liquid state before an excursion to the other state can be made. The relationship between the atomic arrangements in glass with respect to a crystal will be discussed in greater detail in Chapter 3.

Suggested reading: Y. Waseda, *The Structure of Non-Crystalline Materials*, McGraw-Hill Book Co., New York, 1980.

2.4. Anomalies in the $V-T$ Diagram

Figure 2-1 represents the behavior typically observed for a substance which upon cooling from a liquid state either changes into a crystal or moves into the glassy state. It is interesting to raise the question whether, because of the disorder, the volume of glass will always be higher than that of the

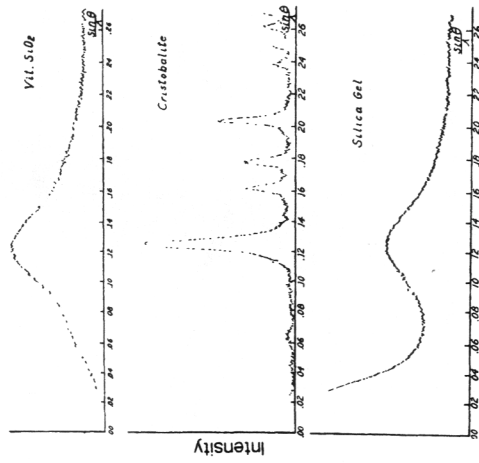


Figure 2-6. Microphotometer records of x-ray diffraction patterns of vitreous silica, cristobalite, and dried silica gel.

corresponding crystal. The answer is, "Not necessarily so!" It is possible to think that a periodic arrangement of atoms could not be accomplished in the most dense form and that the disorder allows a closer packing. An example of this is the water-ice system. It is well known that the densities of ice and water at 0°C are 0.917 g/cm^3 and 0.99987 g/cm^3 , respectively. It is clear that if we could avoid crystallization of water to ice below 0°C and bring the resulting supercooled water to a glassy state (by rapid quenching), the volume of the vitreous water would still be less than that of the ice crystals. Some other examples of this type of behavior are known to exist in tetrahedral glasses such as CdGeAs_2 , eucryptite glass-ceramic [3], and several heavy metal fluoride glasses.

Yet another and somewhat similar question is, "Will the faster-cooled glass always have a higher volume than a slower-cooled glass?" Again, the answer is, "Not necessarily so." It depends upon the shape of the $V-T$ curve in the supercooled liquid region. It happens that the supercooled liquid curve for vitreous silica is V-shaped [4]. Slower and slower cooling causes the supercooled liquid state to move gradually from the right arm to the left arm (see Fig. 2-7). Glasses obtained by cooling from points on the right arm behave "normally," however, those cooled from points on the left arm behave "anomalously." A quickly cooled glass will actually have a lower volume than one cooled more slowly.

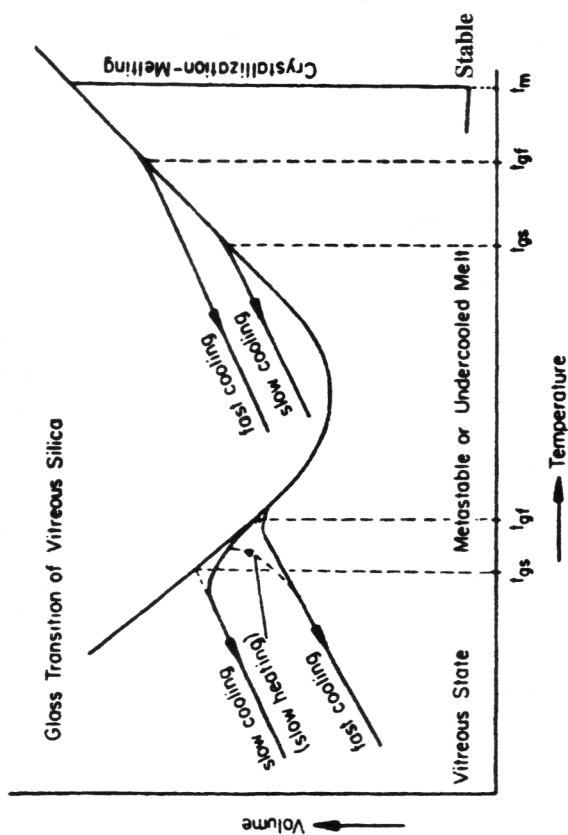


Figure 2-7. Volume versus temperature diagram for low-OH silica glass. t_{gs} , t_{gf} are glass transition temperatures for slow and fast cooling, respectively. (After R. Brückner, *Glastech. Ber.* **43**, 8 (1970).)

The ice-water and the fused silica examples, however, are rare. Fig. 2-1 represents the typical behavior. It is, perhaps, sufficient to recognize that glass maintains the structure, the volume, and hence the energy of a liquid; however, the *changes (or the derivative)* of the energy and the volume with respect to temperature and pressure are similar in magnitude to those in a corresponding crystal.

Exercises

1. Scientists normally classify matter into three groups: solids, liquids, and gases. What property or properties distinguish a solid from a liquid?

(Answer: There is no single physical property that distinguishes a solid from a liquid. A solid should have a "significantly large" shear (rigidity) modulus. A liquid should have "significantly low" viscosity. Much of this is discussed in Chapter 13.)
2. Would you classify the glassy state as the "fourth state of matter"?

(Answer: The three states of matter, viz., gas, liquid and solid, are thermodynamically stable states. By this we mean that any two of the three thermodynamic stable variables P , V , and T uniquely define the third variable. It will be stated in Chapter 13 that glass is not a thermodynamically stable state of matter. Some properties of glasses make them resemble solids; others make them resemble liquids. The distinction in each case is not sufficient to warrant another classification.)

3. Draw a tentative $V-T$ diagram for the ice-water system, clearly showing the formation of glass and the crystal by cooling from the liquid state.
4. Draw a tentative $V-T$ diagram for elemental silicon, showing the formation of the glassy state, the amorphous state, and the crystal by cooling from the liquid state. (Note: This is still a debated topic.)

References

1. J. T. Randall, H. P. Rooksby, and B. S. Cooper, *J. Soc. Glass Technol.* **15**, 54 (1931).
2. B. E. Warren, *J. Appl. Phys.* **8**, 645 (1937).
3. W. Baum, *Glastech. Ber.* **36**, 444 and 468 (1963).
4. R. Brückner, *Glastech. Ber.* **43**, 8 (1970).