

The Physics of Amorphous Solids

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PREFACE

Traditionally, solid-state physics has meant crystal physics. Solidity and crystallinity are treated as synonymous in the standard texts on condensed matter. Yet, one of the most active fields of solid-state research in recent years has been the study of solids that are *not* crystals, solids in which the arrangement of the atoms lacks the slightest vestige of long-range order. The advances that have been made in the physics and chemistry of these materials, which are known as amorphous solids or as glasses, have been widely appreciated within the research community and have contributed to the Nobel awards earned by three individuals (N. F. Mott, P. W. Anderson, and P. J. Flory). Excellent reviews of recent research on these solids have appeared and continue to appear, but relatively little has been written to guide the nonexpert and the student. My aim in writing this book has been to contribute a tutorial presentation of parts of this fascinating subject, a presentation which I hope will be of use as an introduction to newcomers to the field. The level of treatment should make it possible for most of the topics covered to be included in a first-year graduate course on the physics of solids.

Much of the intellectual fascination about the amorphous solid state arises from the fact that scientific insight must be achieved without the help of the mathematical amenities (Brillouin zones, Bloch states, group-theoretical selection rules, etc.) which accompany periodicity in the crystalline solid state. While some old approaches remain useful for amorphous solids (most notably the chemical-bonding viewpoint, which focuses on the short-range order), this challenge has been met mainly by new approaches such as localization theory and percolation. From another viewpoint, much of the intense research interest in amorphous solids is driven by the technological importance of these materials. Examples include the use of ultratransparent optical fibers in telecommunications, the use of amorphous semiconductors in xerography and solar cells, and the ubiquitous everyday uses of organic glasses as structural materials. Applications are discussed in the first and last chapters of this book.

Chapter One deals with certain general aspects, including the *inessentialness* of long-range order in solids, ways in which amorphous solids are formed, the phenomenology of the liquid \leftrightarrow glass transition, and a brief survey of technological applications. Chapters Two and Three deal extensively with structural issues in the various classes of amorphous solids. The atomic-scale structure of an amorphous solid is one of its key mysteries, and structural information must be won with great effort. The stochastic-geometry models which have been found to successfully describe the topologically disordered structures of these solids include the random-close-packing model for simple metallic glasses,

the continuous-random-network model for covalently bonded glasses, and the random coil model for organic polymers. Chapter Four presents a treatment of percolation theory, carried to some depth. The percolation model is a powerful unifying construct and an outstanding vehicle for exhibiting many of the modes of thought characteristic of theoretical approaches to strongly disordered systems: emphasis on statistical distributions, localization \leftrightarrow delocalization critical points, scaling behavior, and dimensionality dependences. It is thus a great help in discussions of physical phenomena in amorphous solids, and is made use of in this way in the last part of the book. Percolation also happens to be a lot of fun, which is another reason why Chapter Four is not short. As a case in point, the scaling approach of phase-transition theory becomes extremely transparent within the context of the percolation model. Scaling ideas recur several times in this book, in connection with polymer structure (Section 3.10), percolation (Section 4.5), politics (Section 4.8), and electron localization (Section 5.7). The final two chapters of the book deal with physical properties of amorphous solids. Topics include theories of the glass transition, Anderson localization and the mobility edge in amorphous semiconductors, optical properties associated with electronic and vibrational excitations, electrical properties of metallic and semiconducting glasses, and chemical-bonding approaches to electronic structure and to the technological control of properties.

My interest in the physics of amorphous solids developed over a period of years within the stimulating environment of the Xerox Webster Research Center, a laboratory that has produced many important contributions to this field. I am indebted to many of my colleagues at Xerox, but I am especially grateful to Harvey Scher, Michael Slade, and Bernard Weinstein, with whom I have had the pleasure of working on diverse aspects of research on amorphous solids. Elsewhere, I wish to thank David Adler, William Paul, and Jan Tauc for many stimulating discussions over the years. The very able and amicable help of Theresa Kusse and Nancy MacDonald in the preparation of the manuscript is gratefully acknowledged. Many of the figures in this book have benefited from the excellent artwork of Lance Monjé. The patient encouragement of Beatrice Shube at John Wiley is also appreciated. Most of all, however, I wish to express my deep appreciation to my wife, Doris, whose indispensable support made the book possible.

RICHARD ZALLEN

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CONTENTS

CHAPTER 1	The Formation of Amorphous Solids	1
1.1	Freezing into the Solid State: Glass Formation versus Crystallization	1
1.2	Preparation of Amorphous Solids	5
1.3	Structure, Solidity, and Respectability	10
1.4	The Glass Transition	16
1.5	Applications of Amorphous Solids	23
CHAPTER 2	Amorphous Morphology: The Geometry and Topology of Disorder	33
2.1	Introduction: Geometry, Chemistry, and the Primacy of Short-Range Order	33
2.2	Review of Crystalline Close Packing	35
2.3	Partial Characterizations of Structures	38
2.3.1	Coordination Number	38
2.3.2	Radial Distribution Function	40
2.3.3	EXAFS	43
2.3.4	Froth—The Honeycomb of Aggregated Atomic Cells	45
2.3.5	Atomic Polyhedra versus Polyhedral Holes	47
2.4	Random Close Packing	49
2.4.1	Empirical rcp Structure	49
2.4.2	Theoretically Derived rcp	51
2.4.3	Characterizations of the rcp Structure	54
2.4.4	Peas in a Pot	56
2.4.5	Dimensionality Considerations and the Extendability of Local Close Packing	58
2.5	Continuous Random Network	60
2.5.1	The Simplicial Graph	60
2.5.2	Mathematical Bonds and Chemical Bonds: The Covalent Graph	60
2.5.3	The Continuous-Random-Network Model of Covalent Glasses	63
2.5.4	Prototype Elemental crn: Amorphous Silicon	67

2.5.5	Prototype Binary crn: Fused Silica	72
2.6	Experimental RDFs versus rcp and crn Models	73
CHAPTER 3	Chalcogenide Glasses and Organic Polymers	86
3.1	Molecular Solids and Network Dimensionality	86
3.2	One- and Two-Dimensional-Network Solids	90
3.3	Compositional Freedom in Chalcogenide Glasses and in Oxides	97
3.4	The 8 - π Rule and the "Ideal Glass"	101
3.5	Topological Defects and Valence Alternation	104
3.6	The Random Coil Model of Organic Glasses	107
3.7	Random Walks, Drunken Birds, and Configurations of Flexible Chains	113
3.8	SAWs, Mean Fields, and Swollen Coils in Solution	120
3.9	Why Overlapping Coils are "Ideal"	127
3.10	Scaling Exponents and Fractal Dimensions	129
CHAPTER 4	The Percolation Model	135
4.1	Introduction	135
4.2	An Example: The Vandalized Grid	136
4.3	The Percolation Path	139
4.4	Applications to Phase Transitions	146
4.5	Close to Threshold: Critical Exponents, Scaling, and Fractals	153
4.6	Trees, Gels, and Mean Fields	167
4.7	Continuum Percolation and the Critical Volume Fraction	183
4.8	Generalizations and Renormalizations	191
CHAPTER 5	Localization \leftrightarrow Delocalization Transitions	205
5.1	Localized-to-Extended Transitions in Amorphous Solids	205
5.2	Dynamic Modeling: Monte Carlo Simulations of the Glass Transition	206
5.3	The Free-Volume Model of the Glass Transition	212
5.4	Free Volume, Communal Entropy, and Percolation	218
5.5	Electron States and Metal \leftrightarrow Insulator Transitions	223

5.6	Disorder-Induced Localization: The Anderson Transition	231
5.7	Scaling Aspects of Localization	242
CHAPTER 6	Optical and Electrical Properties	252
6.1	Local Order and Chemical Bonding	252
6.2	Optical Properties	260
6.3	Electrical Properties	274
6.4	Native Defects and Useful Impurities	289
	Index	297

CHAPTER ONE

The Formation of Amorphous Solids

1.1 FREEZING INTO THE SOLID STATE: GLASS FORMATION VERSUS CRYSTALLIZATION

To begin with, let us suppose that we all know what is meant by the term "solid." (This innocent assumption is less harmless than it appears, and it calls for a bit of discussion, which is to be supplied in Section 1.3.) In a familiar type of thought experiment, often invoked to conceptually analyze the energetics involved in the formulation of a solid, a large collection of initially isolated atoms is gradually brought together "from infinity" until the actual interatomic spacings of the solid are attained. The actual experiment that most closely corresponds to this gedanken experiment involves cooling the vapor of the material until it condenses into the liquid state, and then further gradual cooling of the liquid until it solidifies. Results of such an experiment, for a given quantity of the material, may be represented on a volume-versus-temperature $V(T)$ plot such as the one schematically shown in Fig. 1.1.

Figure 1.1 should be read from right to left, since time runs in that direction during the course of the quenching (temperature-lowering) experiment. A sharp break or bend in $V(T)$ marks a change of phase occurring with decreasing temperature. The first occurs when the gas (whose volume is limited only by the dimensions of the experimental enclosure) condenses to the liquid phase (of well-defined volume, but shape enclosure-determined) at the boiling temperature T_b . Continued cooling now decreases the liquid volume in a continuous fashion, the slope of the smooth $V(T)$ curve defining the liquid's volume coefficient of thermal expansion $\alpha = (1/V)(\partial V/\partial T)_P$. (The experiment is assumed to be taking place at low pressure, $P \approx 0$.) Eventually, when the temperature is brought low enough, a liquid \rightarrow solid transition takes place (with the exception of liquid helium, which remains liquid as $T \rightarrow 0$ in the absence of pressure). The solid then persists to $T = 0$, its signature in terms of $V(T)$ being a small slope corresponding to the low value (relative to that of the liquid phase) of the expansion coefficient α which characterizes a solid.

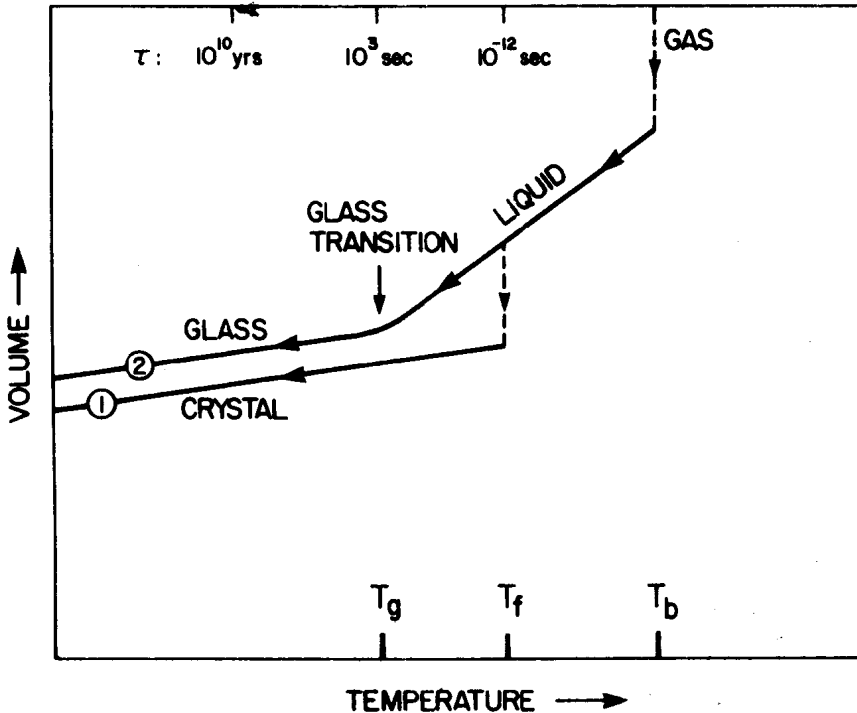


Figure 1.1 The two general cooling paths by which an assembly of atoms can condense into the solid state. Route ① is the path to the crystalline state; route ② is the rapid-quench path to the amorphous solid state.

A liquid may solidify in two ways:

1. *discontinuously* to a crystalline solid or
2. *continuously* to an amorphous solid (glass).

The two solids resulting from these two quite different solidification scenarios are labeled, correspondingly, ① and ② in Fig. 1.1. Scenario ① occurs in Fig. 1.1 at temperature T_f , the freezing (or melting) point. The liquid \rightarrow crystal transition is marked by a discontinuity in $V(T)$, an abrupt contraction to the volume of the crystalline solid. In a quenching experiment carried out at a sufficiently low cooling rate, this is usually the route taken to arrive at the solid state. But at sufficiently high cooling rates, it is found that most materials alter their behavior and follow route ② to the solid phase. T_f is bypassed without incident, and the liquid phase persists until a lower temperature T_g is reached. Here the second solidification scenario is realized. The liquid \rightarrow glass transition occurs in a narrow temperature interval near T_g , the *glass transition temperature*. There is no volume discontinuity, instead $V(T)$ bends over to acquire the small slope (similar to that of the crystal) characteristic of the low thermal expansion of a solid.

Both crystals and glasses are bona fide solids and share the essential attributes of the solid state (Section 1.3). Their fundamental difference is in the basic nature of their microscopic, atomic-scale structure. In crystals, the equilibrium positions of the atoms form a translationally periodic array. The atomic positions exhibit long-range order. In amorphous solids, long-range order is absent; the array of equilibrium atomic positions is strongly disordered. For crystals, the atomic-scale structure is securely known at the outset from the results of diffraction experiments, and it provides the basis for the analysis of such properties as electronic and vibrational excitations. For amorphous solids, the atomic-scale structure is itself one of the key mysteries. Several chapters of this book are devoted to the structure of glasses. A brief preview is given in Section 1.3 and Fig. 1-6.

A note on terminology is in order at this point. The term *amorphous solid* is the general one, applicable to any solid having a nonperiodic atomic array as outlined above. The term *glass* has conventionally been reserved for an amorphous solid actually prepared by quenching the melt, as in ② of Fig. 1.1. Since, as discussed in Section 1.2, there are other ways to prepare amorphous solids than by melt-quenching, glass (in the conventional usage) is the more restrictive term. In this book, that historical distinction will not be adhered to, and both terms will be used synonymously. ("Historical" is used here in two senses, since the distinction itself refers to the history, i.e., method of preparation, of the solid.) Not only does this lubricate the discussion because "glass" is one word while "amorphous solid" is two, it is also convenient to have "glass" to set in opposition to "crystal" (instead of "amorphous solid" versus "crystalline solid"). Other terms, sometimes used in the literature in place of amorphous solid, are noncrystalline solid and vitreous solid.

A detailed view of the vicinity of the liquid→glass solidification transition is shown in Fig. 1.2 for the case of the organic glass polyvinylacetate ($\text{CH}_2\text{CHOOCCH}_3$). The data show results for $V(T)$ obtained at two different cooling rates, and reveal that the observed transition temperature T_g depends upon the cooling rate at which the experiment is carried out. This is a characteristic *kinetic* dimension of the glass transition. The two $V(T)$ curves in Fig. 1.2 are labeled by two experimental time scales, 0.02 hr for the upper curve and 100 hr for the lower curve. In these particular experiments, the stated times are the times elapsed in quenching the specimen to temperature T from a fixed initial temperature well above T_g . Note that the effect of changing this time by a factor of 5000 is to shift T_g by only 8°K. Thus this effect, while quite real, is small.

Denoting the average cooling rate $-\overline{dT/dt}$ by \dot{T} , the mild influence that the time scale of the measurement exerts on the experimentally observed liquid→glass temperature may be indicated by writing T_g as $T_g(\dot{T})$. The weak functional dependence may be approximated as a logarithmic one. Typically, changing \dot{T} by an order of magnitude causes T_g to shift by a few degrees kelvin.

The reason that T_g shifts to lower temperatures when the cooling process is extended over longer times resides in the temperature dependence of a typical

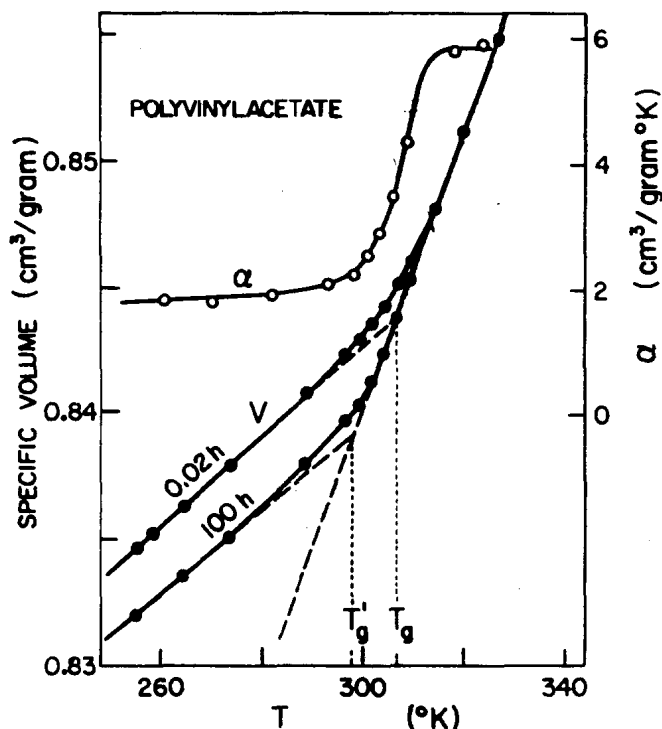


Figure 1.2 Volume-versus-temperature cooling curves for an organic material in the neighborhood of the glass transition. $V(T)$ is shown for two greatly different cooling rates, as is the coefficient of thermal expansion $\alpha(T)$ for the fast-cooling curve (0.02 hr). The break in $V(T)$, and the corresponding step in $\alpha(T)$, signal the occurrence of the liquid→glass transition (after Kovacs, Hutchinson, and Aklonis, 1977).

molecular relaxation time τ . (The adjective “typical” reflects the fact that there is actually a spectrum of relaxation times; τ may be regarded as the geometric mean of that distribution.) The quantity $1/\tau$ characterizes the rate at which the molecular configuration (atomic-scale structure) of the condensed system adapts itself to a change in temperature. This quantity varies enormously during the cooling process. An indication of this dramatic variation is given at the top of Fig. 1.1 where, in crude order-of-magnitude terms, values of τ are associated with three temperatures: T_f , T_g , and a temperature well below T_g (say, $T_g - 50^\circ\text{K}$). The structural-rearrangement response time may increase from the order of 10^{-12} sec at T_f to 10^{10} years (age of the universe) at $T_g - 50^\circ\text{K}$. (Experimentally, τ is accessible at high temperatures where it roughly scales inversely as the viscosity of the liquid. At low temperatures, in the solid, τ is inferred indirectly.)

The 30 orders of magnitude in τ , spanned between the liquid near the melting point and the glass well below the “glass point,” are swept through

swiftly and continuously at temperatures in between. As T traverses the region near T_g , $\tau(T)$ becomes comparable to the time scale of the measurement (typically 10^3 sec, give or take an order of magnitude or two). As T is lowered below T_g , τ becomes much larger than any experimentally accessible times, so that the material loses its ability to rearrange its atomic configuration in harmony with the imposed decline of temperature. The atoms get frozen into well-defined positions (equilibrium positions, about which they oscillate), which correspond to the configuration they had at T_g . It is now easy to understand why, in Fig. 1.2, expanding the experimental time scale (slowing the cooling rate \dot{T}) lowers the observed glass point T_g : If a longer experimental time t is available, then a lower temperature T is needed to achieve the condition $\tau(T) > t$ which freezes the atoms into the configuration that they maintain in the amorphous solid state. Note that the mildness of the t dependence of T_g is simply the other side of the coin with respect to the severity of the exceedingly steep function $\tau(T)$.

While kinetic effects clearly play a role in the operational definition of T_g , it is generally believed that the observed liquid \leftrightarrow glass transition is a manifestation of an underlying thermodynamic transition viewed as corresponding to the limit $t \rightarrow \infty$, $\dot{T} \rightarrow 0$. Some of the experimental evidence of this is given in Section 1.4, and theories of the glass transition—which has been one of the knottiest problems in condensed matter physics—will be discussed in Chapter Four.

In addition to showing what happens to the specific volume (inverse of the density) at temperatures near T_g , Fig. 1.2 also includes a related thermodynamic variable, the expansion coefficient α . This quantity experiences a well-defined “step” near T_g , corresponding to the slope change in $V(T)$. Other thermodynamic aspects of T_g are discussed in Section 1.4.

A comment should be made about the terms “freezing” and “melting.” These two terms are conventionally reserved for the two directions (\leftarrow and \rightarrow) in which a material may traverse the crystal \leftrightarrow liquid transition, the event which occurs at T_f along route ① of Fig. 1.1. This usage is usually adhered to here. But it should be realized that the same terms *also* describe the event that occurs at T_g along route ② of Fig. 1.1. For the glass \leftrightarrow liquid transition, T_g denotes the temperature at which (in direction \leftarrow) the undercooled liquid freezes. In the other direction (\rightarrow , increasing temperature), T_g denotes the temperature at which the glass melts.

1.2 PREPARATION OF AMORPHOUS SOLIDS

For a long time it was thought that only a relatively restricted number of materials could be prepared in the form of amorphous solids, and it was common to refer to these “special” substances (e.g., oxide glasses and organic polymers) as “glass-forming solids.” This notion is wrong, and it is now realized that “glass-forming ability” is almost a universal property of condensable matter. The amorphous solid state is ubiquitous. Table 1.1 presents a list of

TABLE 1.1 Representative amorphous solids, their bonding types, and their glass-transition temperatures

<i>Glass</i>	<i>Bonding</i>	<i>T_g (°K)</i>
SiO ₂	Covalent	1430
GeO ₂	Covalent	820
Si, Ge	Covalent	—
Pd _{0.4} Ni _{0.4} P _{0.2}	Metallic	580
BeF ₂	Ionic	570
As ₂ S ₃	Covalent	470
Polystyrene	Polymeric	370
Se	Polymeric	310
Au _{0.8} Si _{0.2}	Metallic	290
H ₂ O	Hydrogen bonded	140
C ₂ H ₅ OH	Hydrogen bonded	90
Isopentane	van der Waals	65
Fe, Co, Bi	Metallic	—

amorphous solids in which every class of bonding type is represented. The glass-transition temperatures span a wide range.

The correct viewpoint (expressed, for example, in D. Turnbull's 1969 review paper) is the following: *Nearly all materials can, if cooled fast enough and far enough, be prepared as amorphous solids.* ("Fast" and "far" are explained below.) This viewpoint has been abundantly supported in recent years by the preparation of an enormous variety of amorphous solids. Prominent among these, and providing one of the most striking demonstrations of the ubiquity of this state of condensed matter, are the metallic glasses. Because metals tend to be structurally simple materials (many form, in the crystalline state, close-packed structures), the proliferation of glassy metals is a very significant development. Traditional "glass formers" have been materials associated with considerable complexity on a molecular scale, such as organic glasses composed of polymer chains having bulky sidegroups dangling from them. Metals had been thought to be too simple to form glasses.

Figure 1.3 displays an effective technique, known as *melt spinning*, for achieving the very high rate of cooling needed to form a metallic glass. A jet of hot molten metal is propelled against the surface of a rapidly rotating copper cylinder, which is kept cool (room temperature or below). The liquid metal is drawn into a thin film, roughly 50 microns thick ($50\ \mu\text{m} = 0.05\ \text{mm}$). Since the film is so thin, since it is in intimate contact with a large heat sink, and since metals have high thermal conductivity, the liquid cools and solidifies extremely fast. A temperature drop of about 1000°K is accomplished in about a millisecond, i.e., $\dot{T} \approx 10^6\ ^\circ\text{K}/\text{sec}$. The solid film of metallic glass is spun off the rotor, as a continuous ribbon, *at a speed exceeding 1 kilometer per minute.*

Thus the name of the game—the essential ingredient in the preparation of an amorphous solid—is *speed*. A given material may solidify via either of the

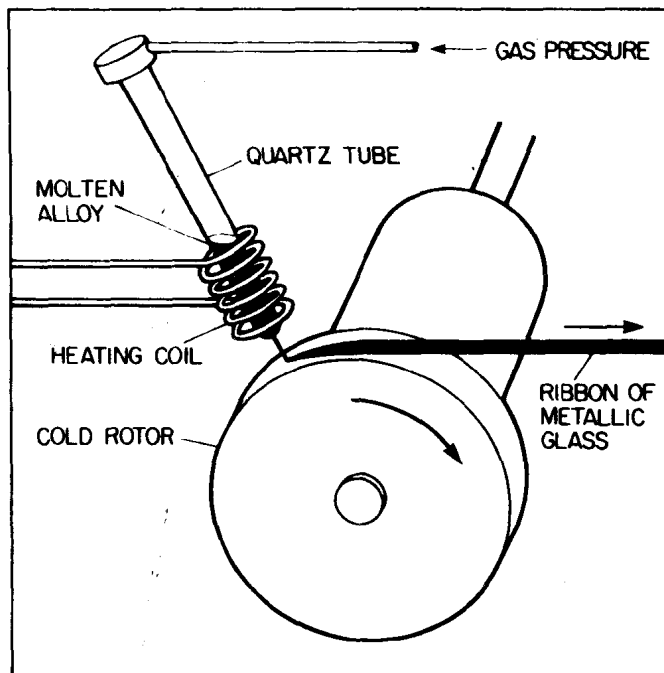


Figure 1.3 Melt spinning of metallic glass. The solid ribbon of amorphous metal is spun off at speeds that can exceed 1 kilometer per minute (from Chaudhari, Giessen, and Turnbull, 1980, copyright 1980 by Scientific American, Inc., all rights reserved, used by permission).

two routes indicated in Fig. 1.1. As soon as the temperature of the liquid is lowered to T_f , it may take route ① to the solid state and crystallize. But crystallization takes time. Crystalline centers must form (a process called nucleation) and then grow by outward propagation of the crystal/liquid interfaces. With the liquid being cooled at a finite rate, the liquid may be taken below T_f along the $V(T)$ trajectory which smoothly continues the curve from higher temperatures. In the temperature interval between T_f and T_g , the liquid is referred to as the undercooled or supercooled liquid. (The undercooled liquid is still unambiguously *liquid* and must not be confused with the glass, as is mistakenly done in a few texts.) If its temperature can be taken below T_g before crystallization has had time to occur, the undercooled liquid solidifies as the glass and remains in this form essentially indefinitely.

Glass formation, therefore, is a matter of *bypassing crystallization*. The channel to the crystalline state is evaded by quickly crossing the dangerous regime of temperature between T_f and T_g and achieving the safety of the amorphous solid state below T_g . Throughout the temperature interval $T_g < T < T_f$, the liquid is "at risk" with respect to nucleation and growth of crystallites. Earlier it was stated that, for a material to be prepared as an amorphous solid, cooling must

proceed "fast enough and far enough." "Far enough" is seen to mean that the quench must be taken to $T < T_g$, and "fast enough" means that $T_g < T < T_f$ must be crossed in a time too short for crystallization to occur. In contrast to crystallization, which is heterogeneous (pockets of the solid phase appear abruptly within the liquid and then grow at its expense), the liquid \rightarrow glass transformation occurs homogeneously throughout the material. This transformation would be observed for any liquid when sufficiently undercooled (i.e., all liquids would form glasses), except for the intervention of crystallization.

"Fast enough" can be, for many materials, very much slower than the quenching rate ($\dot{T} \approx 10^6$ °K/sec) quoted in connection with Fig. 1.3. Unlike the single millisecond taken to quench a metallic glass, the time taken to quench the silicate glass that forms the rigid ribbed disk of the Mt. Palomar telescope was eight months, corresponding to a leisurely \dot{T} of 3×10^{-5} °K/sec. It is much easier to prepare a glass for which a low \dot{T} suffices than it is to prepare one for which a high \dot{T} is needed. Thus, while it is not meaningful to speak of glass-forming solids (since this classification encompasses virtually all materials), it is certainly valid to refer to *glass-forming tendency*. This attribute is correlated with $1/\dot{T}$, and is obviously much greater for oxide glasses than for metallic glasses.

Figure 1.4 schematically illustrates four techniques for preparing amorphous solids that span the range of quenching rates. These techniques are not fundamentally different from those used for preparing crystalline solids; the point is simply that care is taken to quench fast enough to form the glass rather than slow enough to form the crystal.

For materials with very high glass-forming tendency, the melt can be allowed to cool slowly by simply turning off the furnace or by bringing it down in a programmed manner (Fig. 1.4a). Typical cooling rates are in the range from 10^{-4} to 10^{-1} °K/sec. Glasses in this category, among those listed in Table 1.1, are SiO_2 , As_2S_3 , and polystyrene. Thus, although the crystalline form of As_2S_3 is abundant in nature (which had a long time to produce it) as the mineral orpiment, synthetic crystals cannot be prepared from the melt on any experimentally reasonable time scale. The melt always solidifies as the amorphous solid.

Somewhat faster rates are needed to quench a glass such as amorphous selenium, an elemental glass composed of long-chain polymeric molecules. Using an ice-water bath to quench modest volumes of the melt, as indicated in Fig. 1.4b, yields rates in the range 10^1 – 10^2 °K/sec. Se glass can be prepared by this method, as can the Pd-Ni-P metallic glass included in Table 1.1. This metallic glass has a glass-forming tendency high enough to allow it to be prepared in bulk form, rather than the thin-film form characteristic of the other metallic glasses listed in the table.

The technique sketched in Fig. 1.4c is another of the melt-quenching methods (of which the melt-spinning method of Fig. 1.3 is the most spectacular example) developed specifically for metallic glasses. These methods are collectively called *splat-quenching* techniques, and achieve \dot{T} values in the range 10^5 – 10^8 °K/sec. The hammer-and-anvil drop-smasher method of Fig. 1.4c

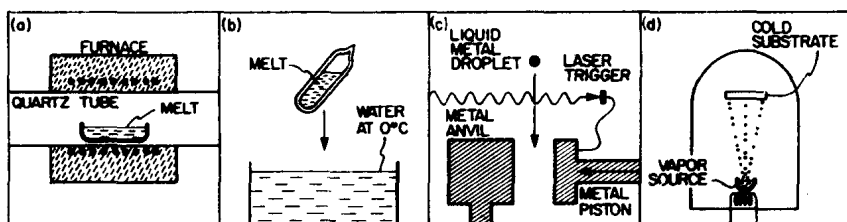


Figure 1.4 Four methods of forming amorphous solids: (a) slow cooling, (b) moderate quenching, (c) rapid "splat-quenching", and (d) condensation from the gas phase.

cools the liquid droplet from two sides at once, and is used to produce milligram-size laboratory specimens of metallic glasses such as the Au-Si alloy listed in Table 1.1.

Before going on to discuss condensation from the vapor phase (Fig. 1.4d), it is interesting to take note of a final method for quenching the liquid, one which is even faster than splat quenching. The technique is called *laser glazing*, and it begins with the material in crystalline form. A very short and very intense single laser pulse is focused onto a very small spot on the crystal surface, with the laser wavelength selected so that the light energy is absorbed in an extremely thin (~ 100 Å) layer of the solid. The large energy dumped into this tiny volume is sufficient to melt it, but it is swiftly quenched and resolidified by the surrounding crystal. The small, very thin, melted-and-quenched region has been found to be amorphous in the case of silicon, a material normally preparable in amorphous form only by vapor-condensation techniques. Amorphous metals can also be prepared by laser glazing. The quench rate can only be roughly estimated by highly approximate calculations; these yield towering \dot{T} values in the range 10^{10} – 10^{12} °K/sec.

All of the glass-forming methods discussed thus far rely upon speed-induced access to route ② of Fig. 1.1. In Fig. 1.4d, we show a representative of a class of techniques that bypasses the liquid phase completely and constructs the amorphous solid in atom-by-atom fashion from the gas phase. These techniques possess the highest effective quench rates (\dot{T} is probably too high to be any longer a meaningful parameter in its original sense), and they are widely used to prepare glasses which have not been obtained by melt-quenching methods.

Figure 1.4d shows the simplest of these *vapor-condensation* techniques. A vapor stream, formed within a vacuum chamber by thermal evaporation of a sample ("source") of the material in question, impinges upon the surface of cold substrate. As the atoms condense on the surface, the as-deposited amorphous structure is quenched in if conditions are arranged so that their thermal energy is extracted from them before they can migrate to the crystalline configuration. Variations of the method involve vaporizing the source by the use of an electron beam, or the use of ion bombardment to drive atoms from it. Another method involves the plasma-induced decomposition of a molecular