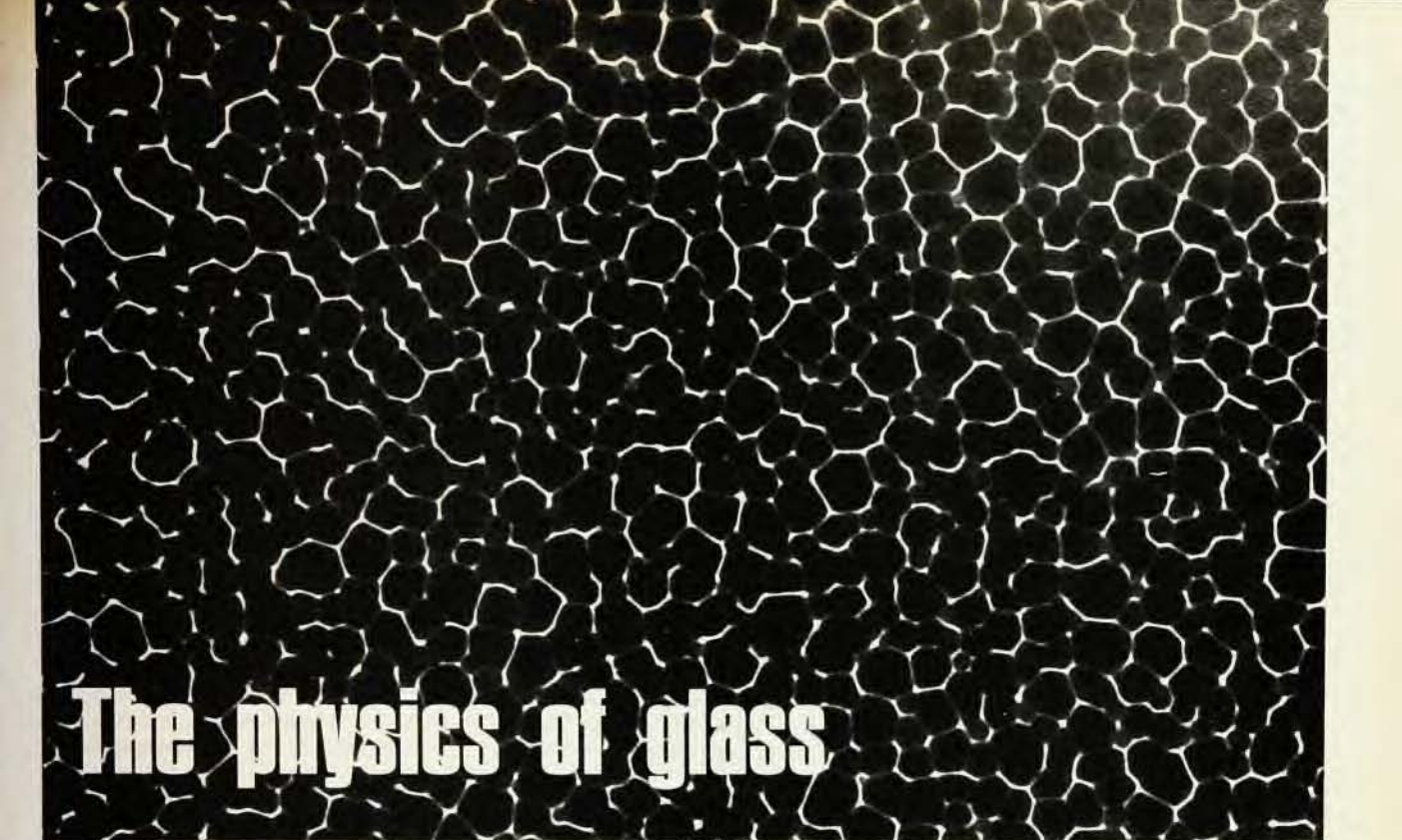




The physics of glass

Our quest for a satisfactory conceptual model of the way crystallization is frustrated in supercooled liquids is still in its infancy, but not for want of experimental data.

James C. Phillips

Some four thousand years ago man discovered glass in the embers of a fire built somewhere in the deserts of the Near East. A few years from now ultratransparent glass fibers will be transmitting more information than copper wires. Thus glass is at once both one of the oldest and one of the newest materials known to civilization. Yet the science of glass is still in its infancy, and the most basic questions remain largely unanswered.

The cause of our scientific ignorance of this material, which has been of so much benefit to mankind, is not want of trying. As early as 1830 Michael Faraday showed that common silicate glass is a solution, not a compound. By 1880 chemists were extensively involved in glass preparation, and by 1930 physicists had begun to study glass structure. Given the sophistication of modern science, which speaks casually of the origin of the universe and the structure of elementary particles on a scale of 10^{-30} centimeters, one would expect that all the basic scientific questions that one might want to raise about glass would have been an-

swered long since. Why has this not happened?

The general answer to this question is that glasses are not in thermal equilibrium and that the atomic structure of glass is not periodic because glasses are not crystalline. In the absence of a periodic structure, such non-thermally-equilibrated material becomes an assembly of interlocking microcosms whose relaxation and organization has been arrested to varying degrees. In effect, a macroscopic glass sample is a universe of regions at different stages of evolution. We are thus confronted with a global problem that in some respects dwarfs in difficulty both cosmology and elementary-particle physics, subjects that are difficult in part because of the practical obstacles encountered in obtaining experimental data. Unlike these subjects, glasses are easily studied experimentally, but translating the experimental data into a satisfactory conceptual model has so far not proved possible. We are thus confronted not with adventitious limitations but rather with the inherent boundaries of our own understanding. As Pogo has so aptly put it, "We have met the enemy, and he is us."

Amorphous materials

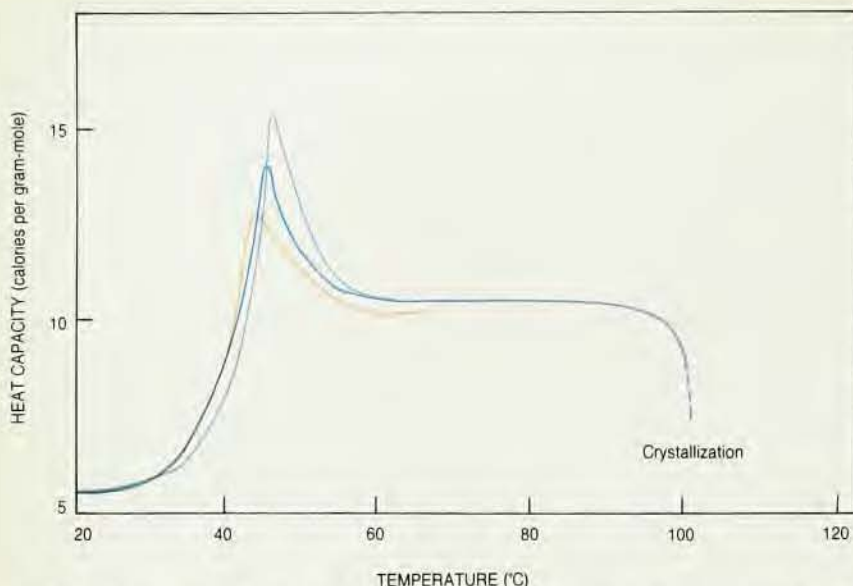
In some way the development of long-range order through crystallization has

Film of glassy As_2Se_3 , 600 Å thick, shows domain structure in this transmission electron micrograph. The bright lines represent troughs in the film that are about 30 Å wide and up to 570 Å deep. The diameter of an average (hexagonal) domain is about 1000 Å (see figure 7). This picture of large-scale structure has the highest contrast and the sharpest definition yet obtained for the microstructure of a thin evaporated film. Figure 1

been frustrated in glass-forming materials by specific structural mechanisms. For organic materials such as glycerine or glucose, which are composed of macromolecules, awkwardness of packing or steric hindrance is sufficient to prevent crystallization. For many inorganic materials the specific mechanism responsible for the avoidance of crystallization is less obvious. Indeed, until quite recently most theoretical physicists felt that the connection between structure and crystallization-suppressing mechanisms in glasses might remain forever inaccessible. However, in the last few years a more optimistic note has been sounded, especially by Nevill Mott and Philip Anderson, that has renewed interest in the entire field of non-crystalline solids. Given the remarkable capabilities of modern instrumentation, we may be close to being able to understand and to predict the properties of glasses on a microscopic scale.

Traditional discussions¹ of the glass-forming tendency in inorganic glasses have focused on thermochemical trends in oxide glasses, especially the borosilicate glasses, which are of greatest importance both historically and

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Heat capacity curves reflect the thermal histories of three samples of 100%-selenium glass. The greater the degree of annealing below the glass transition temperature (about 48 °C), the higher and narrower the peak in a sample's heat capacity curve. (Data from reference 4.) Figure 2

technologically. More recently physicists have focused their attention on semiconductive and metallic glasses,² where the interatomic force fields may be analyzed more simply. This quest for simplicity has also produced extensive discussions of mechanisms that may inhibit crystallization even in supercooled liquids of non-glass-forming materials such as metallic lead. In this article, however, I will discuss mainly the semiconductive glasses, because some of these are very good glass-formers (comparable to silica itself) and yet are still amenable to quantitative treatment on a molecular level.

The central difference between oxide, semiconductive and metallic glasses lies in the relative strengths of their chemical bonds as measured by the energy gap between occupied and unoccupied electronic states. In oxide glasses this gap is more than six electron volts—that is, it lies in the vacuum ultraviolet—so that such glasses are transparent and colorless (apart from impurities). The semiconductive glasses have energy gaps near 1.5 eV and are colored yellow or red, while in metallic glasses the energy gap is, of course, zero.

One of the great unresolved debates in science concerns the microstructure of glass and its connection to crystalline structure. Suppose we consider a glassy material whose composition corresponds to that of a crystalline compound such as the oxide glass SiO_2 or the semiconductive glass As_2S_3 . Most Western scientists have assumed that such glasses, although not crystalline, are continuous on a molecular scale.³ Most Russian scientists,³ on the other hand, believe that on some scale (which

they do not specify) the glasses form clusters that are at most weakly interconnected. They further assert that the topology of these clusters is often crystalline (or "paracrystalline"), although the clusters are both too small and too strained to produce the kind of Laue diffraction patterns that are observed from polycrystalline powders.

Many Western scientists feel uncomfortable with theories that postulate the existence of structures that have not been directly observed. Figure 1 is an enlargement of an electron micrograph of an evaporated film of As_2S_3 that contains clusters of the type predicted by, but never observed by, Russian workers. The diffraction pattern from this film shows the broad rings characteristic of amorphous material; the clusters are very large macromolecules, about 1000 Å in diameter. In this article I will discuss some molecular models that describe how and why these clusters are formed. I will make particular reference to a topological approach that I have found most encouraging.

Properties of glass

Before beginning the mathematical analysis let us first make ourselves feel at home with glasses. The thermal properties of glasses are usually described by a nonequilibrium pseudo-specific-heat function $c(T)$, which is measured by heating a bulk glass sample (about one gram) at a fixed rate, typically around 10 Kelvins per minute. Because the glass is not in thermodynamic equilibrium, $c(T)$ depends weakly on the previous thermal history of the glass and on the calorimetric scanning rate. While this weak second-

dary dependence often causes anxiety in the minds of physicists, materials scientists usually pay it scant attention. The reason for this is that in a series of varying chemical composition the primary dependence of $c(T)$ on composition is usually much greater than its secondary dependence on the thermal history or the scanning rate.

A representative glass transition,⁴ that of bulk selenium glass, is shown in figure 2, illustrating the effect of variable thermal history on the melting of the glass into a supercooled liquid, which occurs near 48 °C. Annealing the material below this glass transition raises and narrows the transition peak. On the other hand, the dependence on composition x in a series of $\text{As}_x\text{Se}_{1-x}$ alloys is shown in figure 3. These alloys have a common thermal history, and the data, of course, are taken with the same temperature scanning rate.⁴

An alert reader will notice a significant feature in figure 3, namely that the width Γ of the glass transition in $\text{As}_x\text{Se}_{1-x}$ alloys is not a monotonic function of x . We may interpret the width as a measure of the microscopic inhomogeneity of the molecular structure of the alloy and as a measure of the clustering of like atoms into groups of variable size. This width $\Gamma(x)$ is shown in figure 4, and the reader will recognize that there is a deep minimum in $\Gamma(x)$ either at or very near $x = 0.40$. One possible explanation for this deep minimum is that the glass contains microcrystallinities of As_2Se_3 (the mineral orpiment), but numerous diffraction studies have shown that this is not the case. A better explanation is that glass for which $x = 0.4$ consists of a minimally chemically disordered covalent network in which arsenic atoms alternate with selenium atoms and there are few clusters of like atoms. This explanation is probably correct, but it is also incomplete, as we shall see.

Having looked at some actual experimental data, we are now entitled to relax a little and play a mathematical game or two. We know that most materials crystallize and that only a few of them form glasses. Often we see materials such as metallic alloys described as glasses even though they must be quenched very rapidly to avoid crystallization. Quenching rates as high as 10^4 K/sec (splat quenching) or even 10^7 K/sec (laser melting with pulse durations of order 10^{-7} seconds or less) may be required. Thus we know that when we look at glasses that can be formed by cooling more slowly than 10 K/min we are looking at materials that are, phenomenologically speaking, quite exceptional. This means that we will need correspondingly exceptional mathematical techniques to characterize abstractly the glass-forming tendency of materials.

What happens to a good glass-forming material when its melt is slowly cooled? Let us take a topological approach. If the glass consists of N atoms embedded in an N_d -dimensional space, then in the $N_d N$ -dimensional configurational space that describes the atomic positions, the initially rapid motion of the system slows down as the temperature is reduced. The viscosity, both macroscopically and on a molecular scale, increases much more rapidly than in normal materials that readily crystallize.

Qualitatively we can explain this behavior by assuming that as the amplitude of the thermal motion is reduced the atoms form molecules, the molecules aggregate into clusters, and these in turn aggregate to form still larger clusters. The velocity of the nonvibrational thermal motion decreases roughly as $N_c^{-1/2}$, where N_c is the average number of atoms in a cluster. This means that as the cluster size increases, cluster motion slows down, with the viscosity of the supercooled liquid reaching a value of order 10^6 poise near the crystalline melting point. If these clusters consist of periodically repeated subunits, then they represent the nuclei that lead to crystallization. Thus the kinetic process by which crystallization is avoided becomes a structural problem: In the liquid, can large clusters be formed whose morphology somehow avoids periodicity?

Evidence from diffraction experiments suggests that for most materials the formation of large noncrystalline clusters is difficult. In network materials—the bond lengths and bond angles—are almost the same in crystalline and noncrystalline solids. This information, of course, does not uniquely determine whether the structure is periodic or aperiodic, but it does caution us that most liquids will tend to crystallize because of the similar characters of short-range order in the supercooled liquid and in the solid.

Random networks or clusters?

The preceding discussion of cluster formation emphasizes the pluralistic evolution of molecular microstructure as the liquid is supercooled and becomes increasingly viscous. At this point some readers may find the comparison between actual glasses and spin glasses helpful. A spin glass is a crystal such as copper in which magnetic impurities such as manganese have been substituted. The magnetic impurities have so low a concentration that we may suppose that they are randomly distributed, and that their spins engage in quantum-mechanical exchange interactions that are equally likely to be negative (favoring parallel

spins) or positive (favoring antiparallel spins). As the temperature is lowered the spins try to order but are only partially successful in doing so, because they are frustrated by the random sign of the exchange interaction.

The "randomness" that is present in a very dilute alloy of manganese in copper (usually less than 1% of Mn) is an illustration of a picture that many authors have tried to develop for covalent and metallic glasses—which are often described as "random" networks or "random" close-packed solids, respectively. Yet it is my view that this terminology is really justified only in the case of very dilute spin glasses. This is because the spin glass is an artificial case in which the constraints of positional order that are imposed extrinsically by the spatial host lattice prevent relaxation of the spin disorder as the systems is cooled. In fact, in many respects I believe that the frustration derived from the maximal randomness of spin glasses represents the antithesis of the kinetic effects that permit deep supercooling and ultimate freezing into the minimally random noncrystalline solid that is a conventional glass. This is because the frustration in native glass-formers arises intrinsically from the particular interatomic forces in the solid itself, not from extrinsic restrictions such as the positional lattice constraints in a spin glass. It seems to me that the idea of

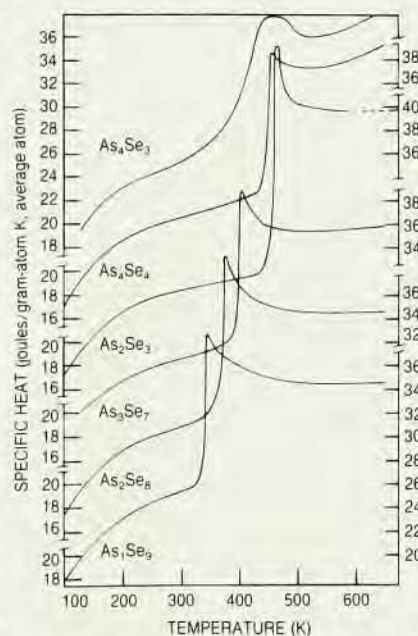
"randomness" in noncrystalline solids has often been used as a means of begging the question, and it is this idea that our topological approach is designed not merely to supplement but actually to replace. The difference in viewpoints is illustrated in figure 5. Incidentally, the idea of continuous random networks in glasses is often ascribed to Frederick William Houlender Zachariasen, but he himself was careful to distinguish between random orientation on a local level and cluster formation on a larger scale.³ The idea of continuous large-scale random networks is thus merely a considerable oversimplification of his ideas.

We can most simply characterize the large clusters topologically by estimating the number of morphologically distinguishable or resolvable clusters (that is, weakly interconnected clusters) that can be made from N_c atoms interacting via $N_c N_i$ interatomic forces, where N_i is the number of interatomic force constraints per atom. We will assume that N_c is so large that we can neglect cluster-surface corrections; this very simple limit is probably never attained in practice, but it is an instructive starting point. There are two cases to consider: $N_c N_i > N_c N_d$ and $N_c N_i < N_c N_d$. An extreme example of the latter case is small molecules, such as I_2 , that can easily crystallize into molecular crystals. In extreme examples of the former case so many constraints are broken that the large excess strain energy will produce a large internal surface area; crystallization of quenched samples may then take place explosively or catastrophically. However, if $N_c N_i$ and $N_c N_d$ are equal, or, equivalently,

$$N_i = N_d \quad (1)$$

we have a condition in which $(N_i - N_d)^2$ is minimized. This condition for mechanical stability may well correspond to the extremal principle that maximizes the sizes of distinguishable clusters and optimizes the glass-forming tendency. Of course, equation 1 as it stands is entirely heuristic, but it does describe mathematically the idea that the awkwardness of molecular rearrangements is the basis for the glass-forming tendency.

In mathematical language we can describe the process of formation of larger and still larger clusters as a contraction or reduction of the dimensionality of the volume of $N_d N$ configurational space accessible during laboratory times to the system as the liquid is supercooled. This procedure, which may also be called "configurational localization by dimensional regression," is the same one used in algebraic topology to generalize the calculus of variations to abstract function spaces such as Hilbert space; this is done by



Specific heats of various arsenic-selenium alloy glasses. The width of the glass transition peak can be interpreted as a measure of the degree of microscopic inhomogeneity in the alloy's molecular structure, or the amount of clustering of like atoms. For As_2Se_3 this width is a minimum, as shown explicitly in figure 4. All alloy samples have common thermal histories. (Data from reference 4.) Figure 3

relating extrema, including saddle points as well as maxima and minima, in spaces of changing dimensionalities. But as abstract and elegant as this analogy may be, and in spite of the fact that it makes equation 1 plausible, it suffers from one very grave problem: How do we actually specify the number of constraints N_i per atom for a real material? Specifying Lagrangian constraints for balls rolling down inclined planes is quite a different matter from counting them on an atomic scale in solids.

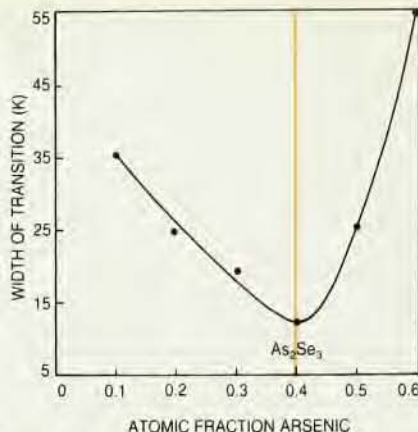
Arsenic-selenium alloys

In general it seems that counting constraints in glass-forming materials is difficult. It is not easy, for example, to list steric constraints for organic macromolecules such as glycerin or glucose or for partially ionic network glasses based on silicon dioxide, where there are significant Coulomb forces of indefinite range. However, there is one family of glasses in which we can actually enumerate constraints, namely the chalcogenide alloys, an example of which is $\text{As}_x\text{Se}_{1-x}$. And from our analogy with variational topology in the large, we can reasonably infer that the principle of dimensional regression describes glass formation in all glass-forming materials. It is therefore important to examine the validity of this principle in the simplest and most favorable circumstances.

By doing a few phenomenological tricks with the periodic table, we can convince ourselves not only that we can count the constraints but that we are indeed on the right track in even thinking about constraints on an atomic scale. There are many different binary combinations of elements from the second through fifth periods and the fourth through sixth columns of this table that might form network glasses with the Coulomb forces sufficiently weak as to be negligible. How do the interatomic forces restrict the allowed configurations in these systems? By examining the known crystal structures, crystal chemists long ago derived certain structural rules, including the following two.

► If A is an element from the fourth or fifth column, and B is an element from the sixth column (sulfur, selenium or tellurium, for example), then the most stable AB structures are the ones in which there are no like-atom nearest-neighbors. That is, the most stable structures are chemically ordered with alternating A and B atoms.

► In many cases the numbers of nearest neighbors—the coordination numbers—of A and B atoms satisfy the so-called $8-N$ rule, where N is the atom's column in the periodic table. According to the rule the sum of N and the coordination number is 8. Arsenic,



Widths of peaks in the specific-heat curves of the arsenic-selenium alloys shown in figure 3. Plotted here are the full widths (measured at half maximum above the liquid plateau) of the glass transitions in the $\text{As}_x\text{Se}_{1-x}$ alloys. The data show a minimum near $x = 0.4$, which is a point of both chemical and mechanical stability (vertical line). Figure 4

for example, with $N = 5$, has 3 nearest neighbors.

These rules are quite useful, but when we systematically examine in detail the crystal structure of all $A^{IV}B_2^{VI}$ and $A_2^{VI}B_3^{VI}$ compounds, we discover a surprising fact, namely that the $8-N$ rule is *always* satisfied for binary A_xB_{1-x} alloys only when A is germanium or arsenic and B is sulfur or selenium. For all the other binary combinations of elements there are compounds in which the $8-N$ rule is violated. In those cases the interatomic forces do not function sufficiently well as constraints to define a unique coordination number.

This is a very interesting observation, because it just so happens that when A is germanium or arsenic and B is sulfur or selenium (but not tellurium, which may have a coordination number of 2 or 3), we get the best inorganic and non-oxide glass-forming binary alloy materials. This could be a coincidence, but the odds against its being so are enormous. We conclude that one can define constraints when there is chemical ordering and a fixed coordination number (given by the $8-N$ rule) and the Coulomb forces are weak. Now we have only to denumerate them.

By far the most accurate and economical characterization of the quantum-mechanical or non-classical interatomic forces in covalent solids is made in terms of the valence force fields that are well known to chemists and molecular spectroscopists. The strongest valence force fields involve bond stretching and bond bending, and the remaining ones are weaker than the residual Coulomb forces. Simple counting shows that the numbers of bond stretching and bending constraints per

atom of coordination number m are $m/2$ and $m(m-1)/2$, respectively. The sum of these two terms, $m^2/2$, gives the number N_i of constraints per atom.⁵ A problem arises, however, in defining m in a binary A_xB_{1-x} alloy. The question is, should we average the coordination number and then square, or should we first square and then take the weighted average? If we average first, the glass-forming condition of equation 1, with $N_d = 3$, gives a universal ideal average coordination number $\bar{m} = 6^{1/2} = 2.45$. Allowing instead for chemical ordering means that we can distinguish the A and B atoms so that we should square first and then take the weighted average. Thus in $\text{As}_x(\text{S or Se})_{1-x}$ alloys, if we give a weight x to the square of arsenic's coordination number and a weight $1-x$ to that of sulfur or selenium, the application of equation 1 gives $x = 0.40$ and $\bar{m} = 2.40$; in $\text{Ge}_y(\text{S or Se})_{1-y}$ alloys, $y = 1/6$ and $\bar{m} = 2.33$. An important feature of this algebraic topological approach is that it considers the coordination number as a continuous rather than an integral variable. It thus leads to insights that cannot be reached with the popular mechanical models of the ball-and-stick type.

Experimental tests

The fact that $\text{As}_x\text{Se}_{1-x}$ alloys are mechanically stable when x is 0.40 is in very good agreement with the deep minimum in the transition width at $x = 0.40$ in figure 4. Thus we see that there may well be *two* reasons for the existence and position of this minimum, namely a chemical one and a mechanical one. Stated differently, the enthalpy of melting is maximized when x is 0.40, producing chemical stability and homogeneity. Moreover, at this value of x the network stress can be minimized because there are enough degrees of freedom to accommodate the interatomic forces. At the same time, the configurational entropy of the glass, that is, the entropy over and above that obtained from the appropriately weighted average of the corresponding crystalline entropies, is minimized when the mechanical condition $N_i = N_d$ is satisfied. Indeed I believe that it is the accidental coincidence of chemical and mechanical extrema that makes it possible for $\text{As}_x(\text{S or Se})_{1-x}$ to be such good glass-formers when x is 0.40 even though a unique, completely unambiguous and even naturally occurring crystalline compound (called orpiment by mineralogists) exists at this composition.

We can make a second test of the topological theory with $\text{Ge}_y(\text{S or Se})_{1-y}$ alloys. Here chemical stability is maximized when y is $1/3$, while mechanical or topological stability is optimized when y is $1/6$. For this system the

theory is most fortunate in having available data on the composition dependence of the minimal quenching rate needed to avoid crystallization, that is, the rate necessary to form a glass rather than a crystalline structure. These data, which reflect measurements at three different quenching rates, are the only ones of this type known to me; they were taken by French experimentalists⁶ and are shown in figure 6. The ordinate here is roughly the logarithm of the quenching rate and "slow cooling" literally means letting the melted sample cool by turning off the furnace. The figure, including the solid curve, is due entirely to the experimentalists, apart from the dashed line that I have added to guide the reader's eye.

This remarkable figure contains a wealth of information concerning the kinetics of glass freezing and the avoidance of crystallization. First we note the rather narrow peaks in the glass-forming difficulty at the two crystalline compositions $y=0$ and $y=1/3$. Although no theory exists, I would be willing to wager that the functional form of these peaks, over and above the dashed background described by the topological theory, reflects the entropy of mixing, which in an ideal solution has the form $|y - y_i| \log |y - y_i|$ for y near y_i . However, these are merely secondary features of the solid curve that are superimposed on the primary trend shown by the dashed line. Note that the minimum in the dashed line occurs at or very near $y = 1/6$, as predicted by the topological theory. This minimum does not arise primarily from eutectic effects, by which we exploit the

entropy of mixing in order more easily to avoid crystallization. Such eutectic effects play only a secondary role in glass-forming materials that are nearly optimally constrained. In fact, I believe that the combination of figures 4 and 6 constitutes decisive evidence in favor of the topological definition of the optimal glass-forming system, equation 1, and shows that the kinetics of supercooling in covalent network glasses are dominated primarily by the average mechanical stress.⁵

Analytical techniques

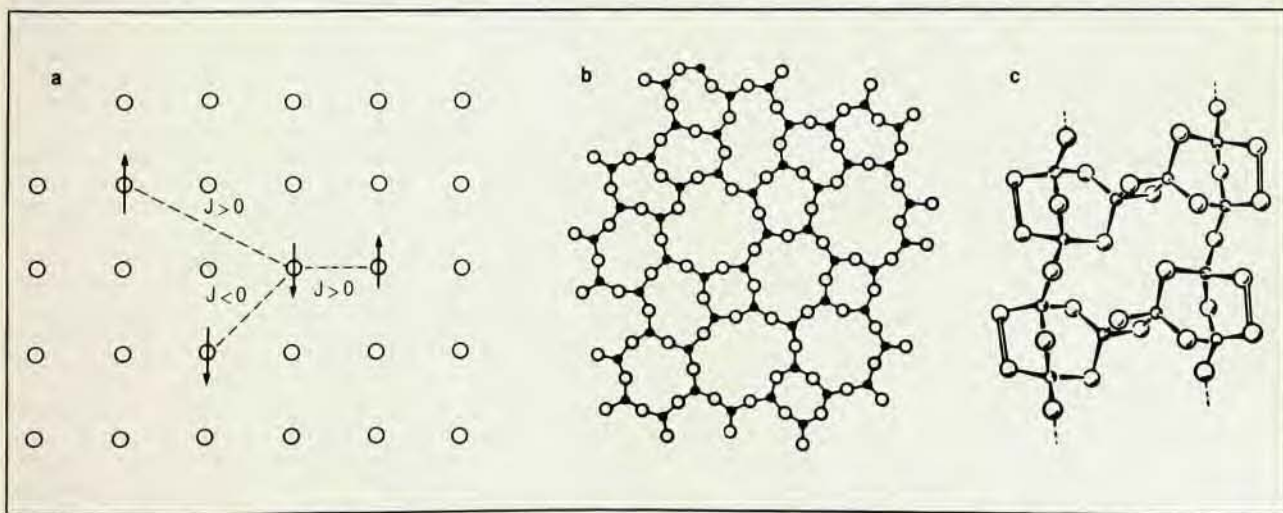
By this time many readers may have found that their interest in this subject has been whetted sufficiently to make them feel dissatisfied with the "merely" thermochemical and kinetic data shown in figures 4 and 6. For my part I feel that a beginning reader, unfamiliar with the phenomenology of glasses and inexperienced in viewing glasses as universes of regions, can easily underestimate the amount to be learned from these figures and from similar phase diagrams that show the composition dependence of the glass transition temperature and the recrystallization temperature on annealing at a constant rate.⁵ On the other hand, there is much to be said for applying to glass science tools from the forefront of the scientific revolution in instrumentation that is currently taking place. Which research tools can we expect to make the greatest contribution to enhancing our understanding of the microscopic morphology of glasses?

On the basis of my personal experience, my answer is Raman scattering and electron microscopy. Raman scat-

tering spectra contain an enormous amount of information, but decoding this information is a major task, the description of which lies outside the scope of this article. I would, however, like to mention the central idea that has emerged recently⁷ from breaking the Raman code in $\text{Ge}_y\text{Se}_{1-y}$ glasses.

One reason for making alloys is that one can enhance the stability of glasses or impede their crystallization by frustrating them chemically. We can do this easily with alloys by choosing a composition between that of two crystalline compositions. In glasses that can be formed only with rapid quenching, such as metallic glasses, this approach has proved very successful. In good formers of network glass this consideration is of secondary importance, as we have just seen. However, evidence is accumulating from Raman scattering that suggests that on the microcosmic level of individual clusters, which may still be partially polymerized to other clusters, chemical ordering becomes imperfect and there are local fluctuations in stoichiometry. In A_xB_{1-x} alloys these lead to the formation of clusters that are locally rich in A or B atoms and contain an excess of $A-A$ or $B-B$ bonds over and above those required by stoichiometry. On a somewhat larger scale, the A -rich clusters to produce maximal chemical stability at the expected formal compositions, such as As_2Se_3 and GeSe_2 .

Of course, we expect a partial breakdown in chemical ordering in the melt. But if this breakdown takes place primarily through only two kinds of cluster morphology, one for A -rich clusters and one for B -rich clusters, then the



Conceptual models of glasses. The ideal spin glass (a) features a low concentration of magnetic moments, which are distributed with maximal randomness on a lattice. The spins are assumed to engage in long-range interactions J with energy that oscillates in sign with distance. The continuous-random-network model (b) is shown here as it applies to B_2O_3 or As_2S_3 glass layers at maximal randomness. The

partially-polymerized-cluster model (c), shown here in the case of GeSe_2 glass, features a sulfur-rich ribbon layer that may be described as a fragment of crystal structure that has been bordered by sulfur dimers (left and right in the figure). These structures are chemically bifurcated but are otherwise minimally disordered. A germanium-rich chain structure may also be described.

Figure 5

configurational entropy associated with such a breakdown is small, as it should be for a good glass-former. Together with large numbers of atoms in a cluster, this mechanism of microcosmic bifurcation strongly enhances the glass-forming tendency. No inconsistency with bulk properties need arise from this mechanism, because the A- and B-rich clusters can associate in the proper proportions, as donor and acceptor molecules do in molecular crystals. For example, the sulfur-rich cluster shown in figure 5c can associate with a germanium-rich cluster to preserve the bulk properties of GeS_2 .

The second technique that has proved to be of great value in extending our understanding of the microstructure of glasses is electron microscopy. This technique is limited to the study of thin samples through which high-energy electron beams can be transmitted without significant absorption or charging. We can sometimes prepare samples of bulk crystals for microscopic study by using various thinning techniques, but this approach is of dubious merit for glasses because of their fragility. Instead we may prepare thin films by vapor deposition, but in doing this we must expect to encounter differences in structure arising from differences in thermal history. In particular, the molecular characteristics of thin films often reflect the vapor-deposition process. Retention of the effects of the preparation process is less of a problem in bulk glasses quenched from a liquid melt. On the other hand, some

of the chemical and mechanical effects we have discussed may be common to both the liquid and the vapor. For example, a certain alloy composition may be both congruently melting and congruently subliming.

Strain: theory and observation

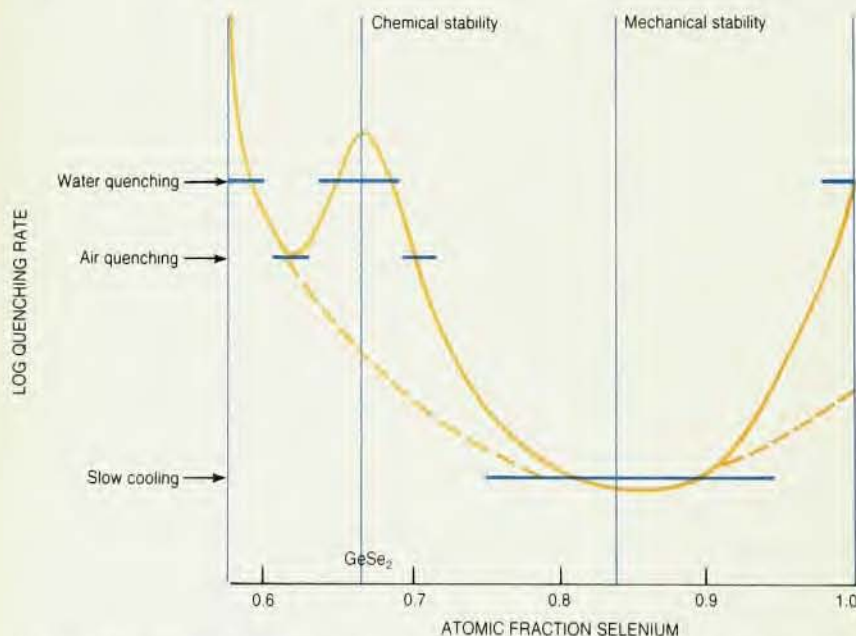
The central implication of the topological model is that at the optimal composition the configurational entropy and the mechanical strain energy of the valence force field are simultaneously minimized. However, this does not mean that the total strain energy is zero, because there are still residual interatomic forces, such as Van der Waals interactions or weak Coulomb interactions, that cannot be completely placated. As a result, when an island of noncrystalline material is nucleated during the vapor deposition of a thin film, we expect strain energy to accumulate as the dimensions of the island increase.

At present there exists no theory of how strain energy accumulates in such an island, although the phenomenon is nearly always encountered in practice when one attempts to construct ball-and-stick models with fixed bond lengths and angles. Only one example of the accumulation of strain energy has been solved explicitly, and this is the planar interface between two crystals with different lattice constants a_1 and a_2 . This geometry gives rise to misfit dislocations, a very anharmonic effect. Yet the strain energy is still proportional to the volume and to

$(a_1 - a_2)^2$, regardless of the magnitude of the formation energy of the dislocation. For this reason we expect that the strain energy in a noncovalent crystalline island of diameter d and thickness t probably increases with the volume or d^2t , and therefore some kind of fracture of the film must occur for sufficiently large values of d .

Recently, fracture of the kind expected from the topological theory appears to have been observed⁸ directly by electron microscopy in thin films of As_{2+u} ($\text{Te}_v\text{Se}_{1-v}$)_{3-u}. In figure 1 we see an electron micrograph of a 600 Å film that displays this new phenomenon in material with u and v both zero. The bright lines represent deep troughs in the film that are nearly normal to the film plane. The troughs form almost linear boundaries and are very narrow (about 30 Å wide) and very deep (only 30 Å thick in part). The average diameter of an average (hexagonal) domain is about 1000 Å.

The microscopic interpretation of this structure is that as the film was deposited, islands were indeed formed, but that when large islands came into contact their coalescence was suppressed because the number of interatomic force constraints per atom (N_i) was equal to the dimensionality of the space in which the atoms are embedded (N_d). That is, the network had neither the slack nor the stress that would have permitted coalescence to take place. (Small islands may coalesce because their molecular weight is not sufficient to fix the local orientation of the networks near their interface.) This statement is, of course, only a conjecture, but it is a conjecture we can test by varying u and v . Increasing v with $u = 0$ means replacement of selenium atoms (for which the constraint that the coordination number is 2 is strictly valid) by tellurium atoms (which have a coordination number of 2 or 3). This mechanical destabilization gives flexibility to N_i and leads to the formation of smaller domains and wider, less-deep troughs. Indeed, for v larger than about $2/3$ the definition of the domains and troughs becomes so poor that the electron micrographs of these films exhibit a dappled columnar growth morphology that is apparently very similar to that of thin films made of non-glass-forming materials such as amorphous silicon. The variations in columnar morphology are considerably more gradual than in domain morphology and the two are easily distinguished. Pictorially speaking, columnar structure is analogous to hills and valleys while domain structure is similar to mesas and canyons. The compositional trends in domain and columnar diameters shown in figure 7 dramatize the critical nature of the domain phenomenon in the good glass-former



Quenching rate necessary to avoid crystallization is a measure of the difficulty of forming a glass. Minimal glass-forming quenching rates are shown here as a function of composition of $\text{Ge}_x\text{Se}_{1-x}$ alloys. The peak indicates that fast quenching is required to avoid crystallization when the germanium-selenium mixture is stoichiometrically balanced for GeSe_2 . Horizontal lines represent the formation of glass. (Data from reference 6.)

Figure 6

As_2Se_3 , for which v is zero and the columns fade out. By contrast, As_2Te_3 is a poor glass-former and the domains and columns are not distinguishable.

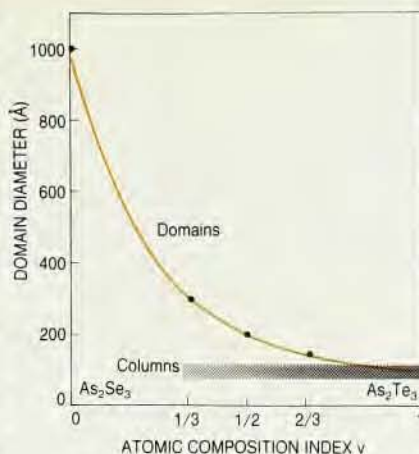
With $v = 0$, increases in $|u|$ as small as 0.05 or less, degrade the trough structure very rapidly even though such increases represent only a 1% change in stoichiometry. Because these chemically destabilizing changes are so small, one must be careful in describing the results. Qualitatively, however, it appears that non-stoichiometric material tends to fill the troughs and at the same time broaden them irregularly from their original width of 30 Å to widths up to 100 Å or more. Perhaps the most decisive feature of this result is that it demonstrates that vapor-phase molecules—of which the most dominant one, As_4Se_6 , corresponds to $u = 0.5$ and $v = 0$ —play little or no role in creating the observed microstructure; their presence can contribute only to its degradation.

How important are chemical and mechanical factors in producing the domain structure? Thin films of GeSe_2 , which are chemically stable but not mechanically stable, do not show the domain structure, nor do films of GeSe_5 , which are mechanically stable but not chemically stable. We conclude that the large-scale structure that is displayed in figure 1 can exist only when by accident the chemical and mechanical conditions for stability are satisfied simultaneously.

Expectation guides observation

The trough structure shown in figure 1 is completely contrary to the common picture of a covalent glass as a continuous random (that is, crystalline) network. Since our choice of experiments is often dictated by what we expect to see, it is perhaps not surprising that this new phenomenon remained unobserved during two decades of active research on chalcogenide glasses and on As_2S_3 and As_2Se_3 in particular. By the same token, however, the discovery of such an unexpected effect calls for deep reconsideration of the tacit assumptions that form the basis of our understanding of dense aperiodic systems. Again some mathematical analogies can be helpful in liberating us from naive preconceptions.

The theoretical explanation of trough formation in terms of mechanical constraints suggests an analogy with misfit dislocations at crystalline interfaces, or with discommensurations of charge density waves. Both of these analogous phenomena occur in lattices as a result of the progressive accumulation of lattice or electronic strain energy, and their calculation in terms of lattice constants is extremely simple.⁹ What is especially striking



Domain diameter as a function of composition in thin films of $\text{As}_2(\text{Te}_v\text{Se}_{1-v})_3$ alloy. As the index v increases, selenium atoms, which have a coordination number strictly equal to two, are replaced by tellurium atoms, which have a coordination number of two or three. This increased flexibility in the number of interatomic force constraints is accompanied by a degradation of the domains and troughs, which become smaller and less deep, respectively. At $v = 1$, they become indistinguishable from mounds and valleys (known as columns) that form in the film. The columns, which are a phenomenon that also occurs in films of non-glass-forming materials, decrease in amplitude as v approaches 0, and therefore are not visible in figure 1. Figure 7

about the troughs in the glass is that they may occur as a result of the accumulation of strain energy without the presence of a lattice reference frame, which is now seen to be merely an incidental computational convenience. Thus each domain forms in a self-limiting manner, and in the absence of domain-domain interactions the domains would be nearly circular and identical in dimensions.

While the semiconductive chalcogenide alloys are the simplest glasses in theory, people have had greatest interest in the oxide glasses, notably the silicates, because of their stability, transparency and ductility. Creep is a common phenomenon and can be observed macroscopically in window glass that has been standing for hundreds of years. It is tempting to suppose that we can explain creep in terms of deformation and translation of domains.

To observe domains in insulating oxide glasses by electron microscopy requires very thin samples to avoid charging. Such samples can be prepared by drawing fibers, but one must then concern oneself with the possible polymerization of the domain interfaces by ambient moisture. By preparing and micrographing samples of silica, germania and silicate glass entirely in an argon atmosphere, some researchers have observed domains of 60–100 Å in diameter.¹⁰ Others have ex-

pressed doubts about these observations because the domain interfaces disappear within a few minutes after exposure to moisture. But one would expect something like this to occur if the domain interfaces near the surface have been enlarged by plastic deformation during sample preparation. Moreover, the small domain size, compared to that of the glassy As_2Se_3 that we saw in figure 1, is again about what one would expect because of the possibility that the cluster surfaces in the oxide glasses are readily formed by coverage with double-bonded oxygen.

The great challenge in the analysis of oxide-glass microstructure today appears to be the decoding of the vibrational spectra of the silicates, especially as measured with very high resolution by Raman spectroscopy. Thanks to the interest in fiber optics, and to the special place of silicates in geophysics, researchers are rapidly producing data on this subject.^{11,12,13} Much remains to be done, however, before theory can catch up with experiment in this fascinating field.

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