

Glass Formation Principles

Suggested reading: H. Rawson, *Inorganic Glass-Forming Systems*, Academic Press, London, 1967.

The preceding discussion indicates that a glass may be made from a crystal by first moving the atoms from their periodic locations to nonperiodic "liquid locations" and then preventing them from falling back into periodic locations. It may be readily realized that fusion of a crystal is an easy way of moving the atoms around. However, it need not necessarily be so (see Section 20.3). The crystal can be dissolved in liquids and reacted until the atoms acquire the desired "liquid locations," and finally the excess solvent can be dried away. This latter process is the basis of glassmaking by the sol-gel route (Section 20.3.3). Likewise, in a vapor deposition technique, the atoms are deposited, nonreactively or reactively, in a disordered manner with or without the use of a substrate that is cold enough to prevent ordering. Some other methods of glassmaking that can be envisioned are bombardment of a crystal by high-energy particles, and shock-induced transformation (Section 20.3.1).

As might be expected, glassmakers' interests have focused on the melting technique since this is suitable for a wide range of compositions and can be used in the laboratory to make glasses on a scale of a few grams and in the plant on a scale of hundreds of tons per day. Table 3-1 shows a partial list

Table 3-1. A Partial List of Glasses Formed by Cooling from a Melt^a

Elements	
S, Se	
Te(?)	
P	
Oxides	B ₂ O ₃ , SiO ₂ , GeO ₂ , P ₂ O ₅ , As ₂ O ₃ , Sb ₂ O ₃ In ₂ O ₃ , Ti ₂ O ₃ , SnO ₂ , PbO ₂ , SeO ₂ "Conditional" TeO ₂ , SeO ₂ , MoO ₃ , WO ₃ , Bi ₂ O ₃ , Al ₂ O ₃ , Ba ₂ O ₃ , V ₂ O ₅ , SO ₃
Sulfides	As ₂ S ₃ , Sb ₂ S ₃ various compounds of B, Ga, In, Te, Ge, Sn, N, P, Bi CS ₂
Selenides	various compounds of Tl, Sn, Pb, As, Sb, Bi, Si, P
Tellurides	various compounds of Tl, Sn, Pb, As, Sb, Bi, Ge
Halides	BeF ₂ , AlF ₃ , ZNCl ₃ , AgCl, Br, I, Pb(Cl ₂ , Br ₂ , I ₂), and multicomponent mixtures
Nitrates	KNO ₃ -Ca(NO ₃) ₂ and many other binary mixtures containing alkali and alkaline earths nitrates
Sulfates	KHSO ₄ and other binary and ternary mixtures
Carbonates	K ₂ CO ₃ -MgCO ₃
Simple organic compounds	O-Terphenyl, toluene, 3-methyl hexane, 2,3-dimethyl ketone, diethyl ether, isobutyl bromide, ethylene glycol, methyl alcohol, ethyl alcohol, glycerol, glucose As droplets only: <i>m</i> -xylene, cyclopentane, <i>n</i> -heptane, methylene chloride
Polymeric organic compounds	
Example—polyethylene (-CH ₂ -), and many others	
Aqueous solutions	
Acids, bases, chlorides, nitrates, and others	
Metallic alloys by "splat cooling"	
Au ₄ Si, Pd ₄ Si	
Te _x -Cu ₂₅ -Au ₅	

^a After R. H. Doremus, *Glass Science*, p. 12. Wiley-Interscience, New York, 1973. Reproduced with permission of J. Wiley & Sons.

of substances that have been brought into glassy state by cooling a melt. Some of these employed ordinary means of cooling (left in air), whereas others required high rates of cooling, for instance, by quenching in a fluid

or pressing between high conductivity surfaces (splat cooling). One clearly needs to inquire what criteria lead to ready glass formation in a given substance. There are two types of theories for glass formation: structural theories, and the kinetic theory. As indicated earlier, most of these theories have been concerned mainly with glass formation in oxides.

3.1. Structural Theories of Glass Formation

There are several structural theories of glass formation: Goldschmidt's radius ratio criterion and Zachariasen's random network theory, both based on coordination number; Smekal's mixed bonding rule and Stanworth's electronegativity rule, both based on bond type; Sun's single bond strength criterion, based on bond strength; Dietzel's field strength criterion; and Phillips' topological constraint model. Some of these are now of historical interest only and are discussed by Rawson. We shall confine our attention to Zachariasen's theory and the latter three.

3.1.1. Zachariasen's Random Network Theory

In a classic paper which, perhaps, has had the most influence on the thinking in glass science, Zachariasen [1] argued that since the mechanical properties of glasses are similar to those of the corresponding crystals, the atomic forces in both must be of the same order. The diffuseness of the x-ray diffraction spectra for glasses clearly indicated that glass itself has an infinitely large unit cell. Glass would therefore consist of a three-dimensional random network. A direct consequence of the randomness would result in glass having higher internal energy than the crystal. Zachariasen believed that this difference in internal energy from that of the corresponding crystal must be small. Otherwise, there would be sufficient driving force towards crystallization. Also, this small energy difference, he suggested, required an open and flexible structure.

In ionic crystals, the cation polyhedra generally share corners. This is particularly true with cations that have a small radius but a high charge. Zachariasen believed that sharing corners is a primary requirement to achieving an open and a random structure. Thus, if a hypothetical compound A₂O₃ could crystallize in two dimensions, then the atomic arrangements in the crystal and the glass should look like those shown in Fig. 3-1. Note that both the crystalline and the glassy forms are composed of AO₃ triangles joined to each other at corners, except that the glassy form has disorder introduced by changes in the A-O-A angles (which are called the bond angles) and slight changes in the A-O bond length. It may also be noted that the

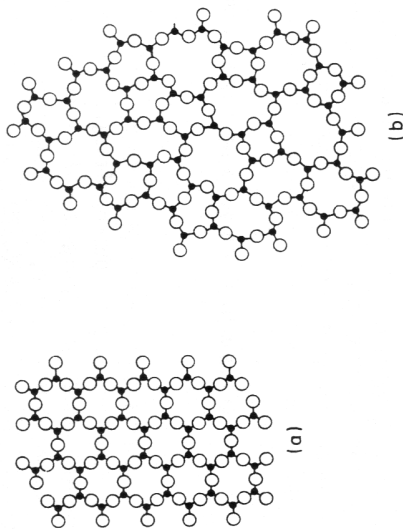


Figure 3-1. Atomic structural representation of (a) A_2O_3 crystal (b) A_2O_3 glass.

triangles or the O–A–O angles themselves need not be deformed much. It is also easy to realize why the compound AO would not form a glass (Fig. 3-2). If the cation polyhedra were triangles, then the coordination of A around O would also be 3. This clearly would imply sharing of oxygen by 3 A's, and hence an ordering would follow simply from topological restraints. Zachariasen therefore defined a glass as a "substance (that) can form extended three-dimensional networks lacking periodicity with an energy content comparable with that of the corresponding crystal network." Accordingly, he laid down **four rules for glass formation** in a compound A_mO_n :

1. An oxygen atom is linked to no more than two atoms of A.
2. The oxygen coordination around A is small, say 3 or 4.
3. The cation polyhedra share corners, not edges, not faces.
4. At least three corners are shared.

Zachariasen stated that whether the atoms are truly ionized or not was of little consequence as long as we could use the ionic interpretation as a convenient means of description. Thus, oxides of the formula A_2O and AO (for cations of group I and II) cannot satisfy many of these rules. For instance, MgO crystallizes in the rock-salt lattice (two interlocking fcc structure). The cations form octahedra that share corners as well as edges. The oxygens are also shared by six cations. Clearly, rules 1–3 are violated, suggesting that glass formation should not occur, as is in fact the case. Rules 1, 3, and 4 are satisfied by any group III oxide A_2O_3 if the oxygens form triangles around A. B_2O_3 is an example of a glass former in this category. (Fig. 3-1b is actually a planar projection or a "pancaked version" of B_2O_3 glass.) Group IV oxides (AO_2), and group V oxides (A_2O_5) would be glass formers if the oxygens formed tetrahedra around the cations. SiO_2 , GeO_2 , P_2O_5 , and As_2O_5 are examples of these. Oxides AO_3 , A_2O_7 , and AO_4 can satisfy rules 1, 3, and 4 if cation octahedra are formed. However, rule 2 would be violated. Oxide MoO_3 does not usually form a glass when melted alone, but glasses containing high percentages of MoO_3 can be made by melting the oxide either with P_2O_5 or with certain other basic oxides.

Zachariasen's random network model received wide support, particularly from the x-ray diffraction work of Warren [2] and his students at MIT. They were easily able to dispel Randall *et al.*'s [3] notion of glass being an assemblage of microcrystals. As stated earlier in Chapter 2, the absence of small-angle scattering in fused silica was used to confirm the absence of any microcrystals such as those found in silica gel. The diffraction spectra from alkali silicate and borosilicate glasses also showed essentially similar features—broad humps at near-neighbor distances (instead of the sharp peaks typical of crystals) and lack of any significant small-angle scattering. As will be discussed in later chapters, Warren and co-workers even showed that the near-neighbor coordinations that could be extracted from the diffraction spectra of various glasses (single-component as well as multicomponent) were essentially in good agreement with the predictions of the random network model.

Support for the random network model in the recent years has come from the work by Cooper [4] using the concepts of topology. As Cooper indicates, Zachariasen's rules 1 and 2 are sufficient to assure geometric freedom to obtain random structures within a closure, and hence they are sufficient to give a low internal energy difference between the glass and the crystal. Rule

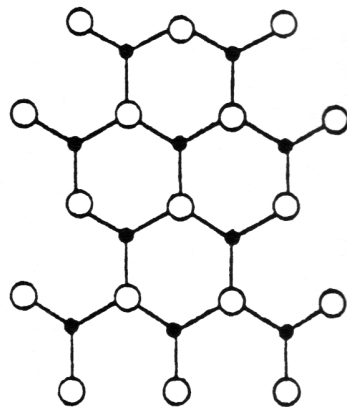


Figure 3-2. Structural representation of a hypothetical crystalline compound AO.

3, which is intended to maximize openness and randomness, may be too stringent. One could include the possibility of edge-sharing by combining rules 3 and 4 and modifying them to state that each oxygen polyhedron must be connected directly to at least three other oxygen polyhedra. Thus, tetrahedra that share an edge and two opposite corners would no longer violate the rules.

Early criticism of Zachariasen's work arose from doubts about whether particular oxides would form glasses or not. Zachariasen himself was not too sure about glass formation in P_2O_3 , As_2O_3 , Sb_2O_3 , V_2O_5 , Sb_2O_5 , Nb_2O_5 , and Ta_2O_5 . In the first three, the oxygens were thought to make octahedra around the cations where three of the oxygens were closer to the cation than the other three. The approximation to a triangular coordination was thought to be the closest in P_2O_3 , and hence the glass-forming capability of P_2O_3 was thought to be the best out of that group. As it turns out, none of these oxides are known to form glasses by ordinary means; however, all of them do form glass networks when a varying quantity of a "stabilizing" modifier oxide is added. In these glasses, the oxygen coordinations of the network forming cation oxide are generally 6-8. (For a recent review of glasses with non-classical glass network forming cations, see Kreidl [5].)

The most important challenge to the random network model came from Lebedev and his Russian co-workers [6,7] who questioned the exact meaning of the word "random." The subsequent discovery of glassy metals, semi-conducting chalcogenides, and heavy metal fluoride glasses that have no oxygens at all required an overhaul in our concepts of "randomly packed" structures. Lebedev and his co-workers' criticism is discussed later in this chapter, and the discussion on the structure of glassy metals is carried out in Chapter 5.

3.1.2. Sun's Single Bond Strength Criterion

Sun [8] suggested that the process of forming a glass had to involve inability to rearrange the bonds in the liquid state during crystallization, and hence, the higher the bond strength the better the glass former. He calculated the strength of the M-O single bond in the oxide $MO_{x/y}$ using the values obtained by Sun and Huggins [9] for the energy E_d required to dissociate the molecule. Shown in Table 3-2 is a summary of his computations. Note that the dissociation energy E_d , for the compound M_yO_x is first divided by y to obtain the energy to dissociate the first coordination sphere and subsequently divided by the coordination number to obtain the strength of the single bond. Where the coordination number is known to change, the values of the single bond strength are computed for the different coordinations. In some cases, such as P, As, V, and Sb, the elements are thought to

Table 3-2. Single Bond Strengths for Oxides^a

	M in MO_x	Valence	Dissociation energy E_d per MO_x (kcal)	Coordination number ^b	Single-bond strength (kcal)	
Glass formers	B	3	356	3	119	
	Si	4	424	4	106	
	Ge	4	431	4	108	
	Al	3	402-317	4	101-79	
	B	3	356	4	89	
	P	5	442	4	111-88	
	V	5	449	4	112-90	
	As	5	349	4	87-70	
	Sb	5	339	4	85-68	
	Zr	4	485	6	81	
	Intermediates	Ti	4	435	6	73
		Zn	2	144	2	72
Pb		2	145	2	73	
Al		3	317-402	6	53-67	
Th		4	516	8	64	
Be		2	250	4	63	
Zr		4	485	8	61	
Cd		2	119	2	60	
Modifiers		Sc	3	362	6	60
		La	3	406	7	58
		Y	3	399	8	50
		Sn	4	278	6	46
	Ga	3	267	6	45	
	In	3	259	6	43	
	Th	4	516	12	43	
	Pb	4	232	6	39	
	Mg	2	222	6	37	
	Li	1	144	4	36	
	Pb	2	145	4	36	
	Zn	2	144	4	36	
	Ba	2	260	8	33	
	Ca	2	257	8	32	
	Sr	2	256	8	32	
	Cd	2	119	4	30	
	Na	1	120	6	20	
	Cd	2	119	6	20	
	K	1	115	9	13	
	Rb	1	115	10	12	
Hg	2	68	6	11		
Cs	1	114	12	10		

^a After Sun [8].

^b Based on either known or assumed values.

be surrounded by three singly bonded oxygens and one doubly bonded oxygen. Thus, two values for the single bond strength were computed corresponding to apparent coordinations of 4 and 5. It can be seen that oxides where the single bond strength exceeds about 80 kcal/mol ($\sim 334 \text{ kJ} \cdot \text{mol}^{-1}$, note $1 \text{ cal} = 4.18 \text{ J}$) could be thought of as **glass network formers (NWF)**. Oxides where the single bond strength was less than about 60 kcal/mol were the **glass network modifiers (NWM)**, and those having values between 60 and 80 kcal/mol were obviously the **intermediates**.

An important contribution made by Sun was the introduction of an "intermediate" category. Many binary glasses have now been prepared where one of the "non-classical" network-forming oxides is the "network-forming" majority constituent: the presence of the second minority oxide acts to stabilize the glass. (For a review, see Ref. 5.)

The most serious problem with Sun's classification is the exclusion of the entire range of chalcogenide glasses where the single bond strengths are generally of the order of only about 40 kcal/mol along the chain (covalent bond) and less between the chains (van der Waals forces). Likewise, a similar problem exists in explaining the glassy metals. In CO_2 , the dissociation energy of the molecule is about 480 kcal/mol, which gives the strength of the single bond to be about 120 kcal/mol (CO_2 may be written as $\text{O}=\text{C}=\text{O}$). The absence of ready glass formation in CO_2 is attributed to the weak van der Waals forces between the CO_2 molecules, which encourage rearrangement to yield crystallization. Despite these several obvious difficulties, the classification of substances into three divisions with regard to their glass-forming ability has been the most important contribution of Sun's single bond strength criterion.

Rawson [10] suggested that the ability for structural rearrangements to occur during crystallization should be determined by the ratio of the bond strength to the energy available at the freezing point. Since the kinetic energy itself is roughly $\frac{3}{2}RT_m$, an appropriate parameter to compare would be B_{M-O}/T_m . The higher the value, the lower the probability for bonds to break at the T_m , and hence the higher the tendency for glass formation. Rawson's most important contribution was to point out the significance of the liquidus temperature in binary and multicomponent systems that, hitherto, had been ignored almost entirely. Glass formation in such systems could be easier if the oxides formed a eutectic at temperatures lower than the melting point of any of the constituent oxides.

3.1.3. Dietzel's Field Strength Criterion

The field strength F of a cation is given by

$$F = Z_c / (r_c + r_{O-})^2 = Z_c / a^2, \quad (3.1)$$

Table 3-3. Field Strengths of Various Ions^a

Element	Valence Z	Ionic radius (for CN = 6) r in Å	Most frequent coordination number CN	Ionic distance for oxides a in Å	Field strength at distance of O^{2-} ions Z/a^2	Function in glass structure
K	1	1.33	8	2.77	0.13	Network modifier $Z/a^2 \approx 0.1 \dots 0.4$
Na	1	0.98	6	2.30	0.19	
Li	1	0.78	6	2.10	0.23	
Ba	2	1.43	8	2.86	0.24	
Pb	2	1.32	8	2.74	0.27	
Sr	2	1.27	8	2.69	0.28	
Ca	2	1.06	8	2.48	0.33	
Mn	2	0.91	6	2.23	0.40	
Fe	2	0.83	6	2.15	0.43	
Mn	2	0.83	4	2.03	0.49	
Mg	2	0.78	6	2.10	0.45	Intermediate $Z/a^2 \approx 0.5 \dots 1.0$
			4	1.96	0.53	
Zr	4	0.87	8	2.28	0.77	
Be	2	0.34	4	1.53	0.86	
Fe	3	0.67	6	1.99	0.76	
			4	1.88	0.85	
Al	3	0.57	6	1.89	0.84	
			4	1.77	0.96	
Ti	4	0.64	6	1.96	1.04	
B	3	0.20	4	1.50	1.34	
Ge	4	0.44	4	1.66	1.45	Network former $Z/a^2 \approx 1.5 \dots 2.0$
Si	4	0.39	4	1.60	1.57	
P	5	0.34	4	1.55	2.1	
B	3	0.20	3	1.36	1.63	

^a After Dietzel [11].

where Z_c is the valency of the cation, and r_c and r_{O-} are the ionic radii of the cation and the oxygen ion in Å units. If e is the electronic charge, then Fe^2 is the force exerted by the cation on a unit point charge placed at the location of the oxygen ion. Values of the field strength for the various ions are shown in Table 3-3.

According to Dietzel [11], the network-forming cations have high field strengths (~ 1.3 to 2), the network-modifying cations have low field strengths (0.1 to 0.4), and those having F values, between 0.5 and 1.1 are the intermediates. Apparently, the high-field-strength cations repel each other strongly. At the same time, their small size requires low-coordination-number polyhedra with the oxygen. The two factors promote disordered arrange-

ments. The low-field-strength cations, on the other hand, can come close to each other and force periodicity of their high-coordination polyhedra. In binary melts, there presumably is a "struggle for oxygen." The coordination requirements for the high-field-strength cations are met first.

Dietzel's field strength argument has been important; however, it clearly is inapplicable to non-ionically bonded solids.

3.1.4. Phillips's Topological Constraints Hypothesis

This is the only concept aimed specifically at estimating glass formability in covalently bonded solids such as the chalcogenides. The coordination of a covalently bonded atom is given by Mott's "8-N" rule or the octet rule [12], according to which the coordination number $m = 8 - N$, where N is the number of valence electrons. Thus, $m_S = m_{Se} = m_{Te} = 2$; $m_{As} = m_{Sb} = 3$; $m_{Si} = m_{Ge} = 4$. The average coordination number $\langle m \rangle$ for a covalently bonded alloy $A_a B_b C_c$ is then given by

$$\langle m \rangle = [am_A + bm_B + cm_C]/(a + b + c). \quad (3.2)$$

For example, $\langle m \rangle_{As_2Se_3} = 2.4$, and if we assume a fully covalent bond in SiO_2 , then $\langle m \rangle_{SiO_2} = 2.67$. In essence, $\langle m \rangle$ is the coordination of a pseudo-atom that would form a structure having the same topology as the complex system.

In the valency-force-field model, a covalently bonded atom experiences bond-stretching (the α type) and bond-bending (the β type) interactions such that the total potential energy, U , is given by

$$U = \left(\frac{1}{2}\right)\alpha\Delta r^2 + \left(\frac{1}{2}\right)\beta r_0^2\Delta\theta^2, \quad (3.3)$$

where Δr and $\Delta\theta$ are changes in the interatomic spacing and bond angle, respectively, from the equilibrium values r and θ . In a binary alloy $A_x B_{1-x}$ there is one bond-stretching interaction and two bond-bending interactions (angles BAB and ABA). Each of these interactions is essentially a force constant that provides a mechanical constraint.

Phillips [13] assumed these mechanical interactions to be rigid over a short-range order, i.e., the bond length r_{AB} , and the next-nearest neighbor distances r_{AA} and r_{BB} were assumed to have zero deviations from the equilibrium values. He then suggested that the *glass-forming tendency is maximized when the number of mechanical constraints N_c equals the number of degrees of freedom N_d* .

For a pseudo-atom in a covalently bonded solid with average coordination number $\langle m \rangle$, the number of α interactions is given by $\langle m \rangle/2$ (the division by 2 is performed to avoid double counting), and the number of β interactions

is $\langle m \rangle(\langle m \rangle - 1)/2$ (the number of combinations out of m neighbors taken two at a time). Hence,

$$N_c = \langle m \rangle/2 + \langle m \rangle(\langle m \rangle - 1)/2 = \langle m \rangle^2/2. \quad (3.4)$$

Equating this to the allowed degrees of freedom, which is 3 (the dimensionality of the system), we get

$$\langle m \rangle^2/2 = 3 \quad \text{or} \quad \langle m \rangle_c = 2.45. \quad (3.5)$$

This is the "universal" critical average coordination number most favorable for glass-forming capability.

For a real system such as $As_x Se_{1-x}$ or $Ge_y Se_{1-y}$, it is more instructive to compute the constraints for each of the atoms first rather than to average the coordination number. For $As_x Se_{1-x}$, this can be done as follows:

$$m_{As} = 3; \quad m_{Se} = 2$$

$$N_c(As) = xm_{As}/2 = 9x/2;$$

$$\text{For Se:} \quad N_c(Se) = (1-x)m_{Se}^2/2 = 2(1-x).$$

Hence, the total number of constraints $N_c = 9x/2 + 2(1-x)$. Setting this equal to 3 ($= N_d$), we get $x = 0.4$, which yields

$$\langle m \rangle_c = 2.40. \quad (3.6)$$

Likewise, for the $Ge_y Se_{1-y}$ alloy, we get

$$N_c = 4^2 y/2 + 2^2(1-y)/2 = 3,$$

or $y = \frac{1}{6}$, which gives

$$\langle m \rangle_c = 2.33. \quad (3.7)$$

Phillips plotted the glass-forming difficulty (the magnitude of the minimum quenching rate required to obtain a glass over a reasonable time) as a function of the alloy composition in the Ge-Se system (Fig. 3-3) and showed that, indeed, the vicinity of 16 mol. % Ge had the least glass-forming difficulty. The solid curve in Fig. 3-3 was separated into a primary parabola (dashed curve) plus secondary peaks at $y = 0$ and at $y = 0.33$ (composition $GeSe_2$). The primary curve represented the effects of the short-range order on the topology and the medium-range order of the covalent network. The secondary peaks represented the effects of the long-range order, i.e., the need to avoid chemical ordering in the vicinity of the crystalline compounds.

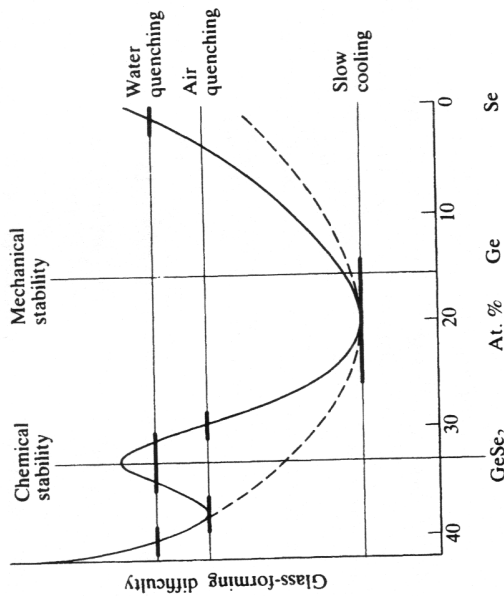


Figure 3-3. Glass-forming difficulty versus composition in the Ge-Se system. Solid horizontal bars are experimental data for the three cooling rates employed (rapid using water, medium using air, and slow cooling). Solid curve is drawn to guide the eye. Dashed curve is the prediction from Phillips' constraint theory. (After J. C. Phillips, *J. Non-cryst. Sol.* **34**, 153 (1979). Reproduced with permission of Elsevier Science Publishers.)

When $\langle m \rangle$ is less than $\langle m \rangle_c$, the glass is "underconstrained" and is appropriately called a "polymeric glass" having large "floppy" or "spongy" regions with a few rigid inclusions. On the other hand, covalent random networks having $\langle m \rangle$ greater than $\langle m \rangle_c$ are "overconstrained" and are best termed "amorphous solids" having large rigid regions with a few "floppy" inclusions (14).

According to Döhler *et al.* [15], Eq. (3.6) is correct for $\langle m \rangle \leq N_d - 1$, but needs to be modified when $\langle m \rangle > N_d - 1$. This is because the $N_d + 1$ angles in N_d dimensions are not linearly independent. The constraint equations should read:

$$N_c = \langle m \rangle / 2 + \langle m \rangle (\langle m \rangle - 1) / 2 \quad \text{for } \langle m \rangle \leq N_d - 1, \quad (3.8)$$

$$N_c = \langle m \rangle / 2 + (N_d - 1)(2\langle m \rangle - N_d) / 2 \quad \text{for } \langle m \rangle > N_d - 1. \quad (3.9)$$

Setting $N_c = N_d$ yields

$$\langle m \rangle_c = (2N_d)^{1/2} \quad \text{for } \langle m \rangle \leq N_d - 1$$

and

$$\langle m \rangle_c = N_d(N_d + 1) / (2N_d - 1) \quad \text{for } \langle m \rangle > N_d - 1.$$

For a 3-D solid and $\langle m \rangle > 2$, Eq. (3.9) gives $\langle m \rangle_c = 2.40$.

In addition to the modification of the number of constraints, Döhler *et al.* also pointed out that substantially polarizable ions would add "internal degrees of freedom" to the N_d . Likewise, the presence of van der Waals forces would tend to increase the effective coordination as well as the internal degrees of freedom due to polarizability.

Many of the topological concepts advanced by Phillips, Thorpe, Döhler *et al.*, and others are quite recent and not fully understood. As a result, they remain as yet inadequately tested. No doubt, a great deal of insight into the glass-forming tendencies of covalently bonded systems and their properties has already been gained through these topological principles. Some of these will be picked up in the discussion of the rigidity properties of the chalcogenides.

3.2. Russian Workers' Criticism of Zachariassen's Hypothesis

Suggested reading: E. A. Porai-Koshits, *J. Non-cryst. Sol.* **123**, 1-13 (1990).

As we mentioned earlier, of all the structural-characteristics-based hypotheses of glass-forming criteria, Zachariassen's random network model had the most impact on scientific thought. The challenge to this model, primarily from Lebedev, Valenkov, Porai-Koshits, and other Russian workers, was focused on the issue of the extent of randomness. Because of the chemical bonding, some ordering is clearly expected. For instance, a silicon atom has to have four oxygens as its first near neighbors, and not two or six oxygens, and definitely not other silicons. The oxygen, in turn, would be bonded to silicons. The number of second near-neighbors for a silicon would hence be somewhat similar to that in a corresponding crystal. The question is, "To what extent is this similarity to the crystalline order extended in a glass?"

Lebedev and coworkers suggested that the structure of a glass was not as random as Zachariassen had postulated, but that there was *evidence of definite short-range structures similar to those found in crystals*. (In chronological terms, Lebedev's view existed 10 years prior to Randall *et al.*'s microcrystals model, and 11 years prior to Zachariassen's random network model.) According to Lebedev:

- A silicate glass is an accumulation of submicrocrystalline formations of various silicates and silica, called "crystallites."

- These crystallites are definite chemical compounds or solid solutions: their chemical nature is determined by the phase diagram for the system that constitutes the glass.
- The crystallites are separated by amorphous layers in which the degree of disorder increases with the distance from the microcrystalline region.
- The crystallites are not mere fragments of a crystal lattice. In reality, they are considerably deformed structural formations with more or less pronounced features of a crystal lattice.

The schematics of the crystallite morphology according to Lebedev are shown in Fig. 3-4. Note the essential difference of their ideas from those of Randall *et al.* Whereas the latter had suggested that a glass was simply an assemblage of finely divided (micro) crystals, Lebedev and coworkers had advanced the idea that the structures of these seemingly crystalline regions were deformed rather than perfect lattices. Thus, a $22\text{Na}_2\text{O}\cdot 78\text{SiO}_2$ (mol. %) glass could be thought to be composed of SiO_2 , $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$, and $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$ crystallites in various percentages, depending upon the phase diagram (and the cooling conditions).

The most important experimental evidence put forward was from XRD. They showed that the radial distribution functions (RDFs) of a borosilicate glass measured using x-rays could simply be constructed by adding individual RDFs of B_2O_3 and SiO_2 in appropriately weighted proportions (see Fig. 3-5a). Likewise, if the RDF of SiO_2 were multiplied by y and subtracted

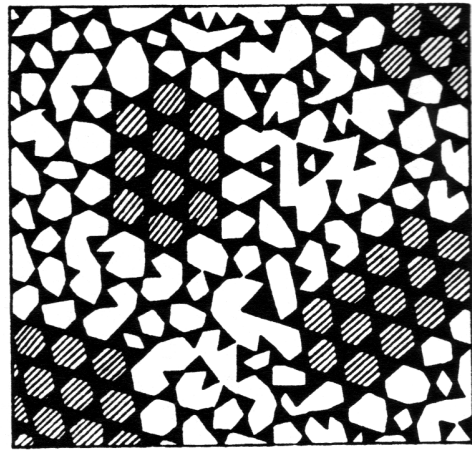


Figure 3-4. Schematic diagram of Lebedev's crystallite theory. Regions of local order (crystallites) are separated by regions of disorder.

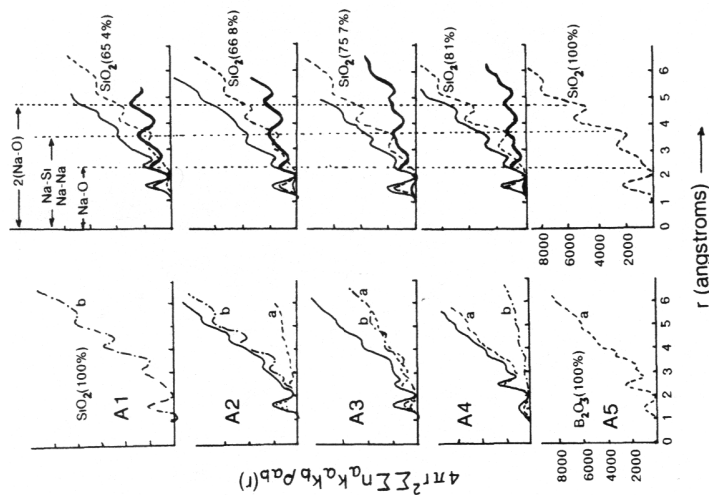


Figure 3-5. RDFs of (A) borosilicate and (B) binary sodium silicate glasses. The ordinate in each case is the pair distribution function, and the abscissa is the radial distance (\AA). In (A), the measured RDF (solid line) of glasses A2 ($= 83.3\text{SiO}_2\cdot 11.5\text{B}_2\text{O}_3\cdot 4\text{Na}_2\text{O}\cdot 1.2\text{Al}_2\text{O}_3$; mol. %), A3 ($= 48.7\text{SiO}_2\cdot 51.3\text{B}_2\text{O}_3$), and A4 ($= 16.9\text{SiO}_2\cdot 83.1\text{B}_2\text{O}_3$) are shown to be the weighted sum of the RDFs of glasses A5 ($= 100\%$ B_2O_3 , marked "a") and A1 ($= 100\%$ SiO_2 , marked "b"). In (B), the RDF of the silica fraction is subtracted out to show that the residual (heavy line) in each case represents Na_2O , which is roughly the same in each case. [Redrawn in portion for clarity from E. A. Porai-Koshits in *The Structure of Glass I*, pp. 29 and 31, Consultants Bureau, New York, 1958. Reproduced with permission of Plenum Press.]

out of the RDFs of various $x\text{Na}_2\text{O}\cdot y\text{SiO}_2$ glasses, then the residuals (indicative of the distribution of Na) had essentially similar shape, suggesting that compounds of sodium present were of similar type in all the different glasses (see Fig. 3-5b).

By 1958, replica electron microscopy of freshly fractured glass surfaces, pioneered by Vogel [16], showed clear evidence of surface "roughness" uncharacteristic of a random, homogeneous phase. An example of this

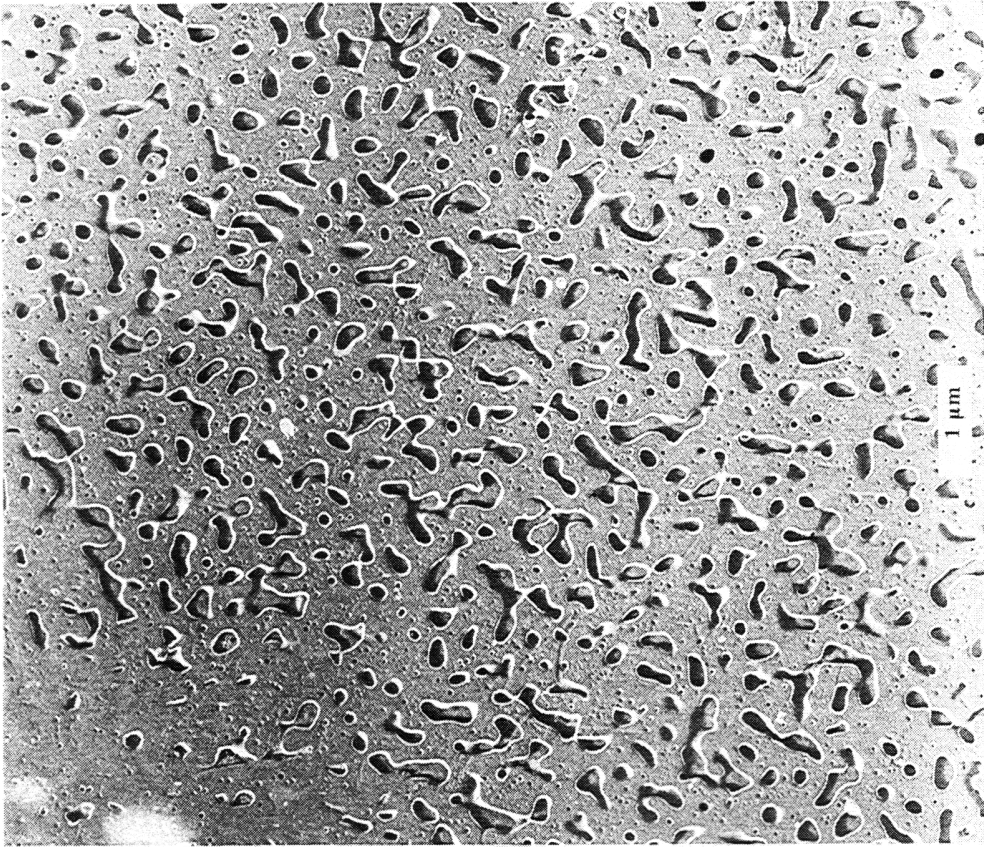


Figure 3-6. Replica transmission electron micrograph of phase separation in $77\text{B}_2\text{O}_3 \cdot 18\text{PbO} \cdot 5\text{Al}_2\text{O}_3$ glass. (Photograph Courtesy of W. Dumbaugh, Corning Inc., Corning, New York.)

so-called **microstructure** (more appropriately, the **nanostucture**) is shown in Fig. 3-6. (To prepare a replica, see Section 4.3.)

No evidence of a microstructure could ever be found in replicas of fused silica. It became clear that *the degree of randomness varied from glass to glass*: some were closer to Zachariasen's picture, while others had more

microcrystalline-type, but not necessarily "crystalline," inhomogeneities. The understanding of the occurrence of such large degree of variations was achieved once the kinetic theory of glass formation and the concepts of phase separation and liquid immiscibility were understood. The kinetic theory is discussed next: phase separation and liquid immiscibility are discussed in the next chapter.

3.3. The Kinetic Theory of Glass Formation

It is generally agreed that many of the liquids that would otherwise crystallize during normal cooling can be brought to a glassy state by a more rapid cooling. We should recognize that the question, "Which compounds can form glass?" is only academic; the real question ought to be, "At what rate should a given liquid be cooled to bring it into a glassy state?" It is now well established that *all liquids*, including water and molten metals, *can be vitrified provided that the rate of cooling is rapid enough to avoid crystallization (also called devitrification) below the freezing point*. Crystallization requires first the formation of a measurable number of nuclei, and *then* the occurrence of a measurable crystal growth rate. Note the emphasis on the sequence of events. In some situations, there may be sufficient nuclei present at the surface. In such cases, a small crystal growth rate could lead to detectable crystallization. To avoid crystallization, one needs to avoid either or both of the two. The following steps are needed to determine whether a system will form a glass (i.e., will not have a certain minimum volume fraction crystals):

1. Calculate the rate of nucleation, I , as a function of temperature.
2. Calculate the rate of crystal growth, u , as a function of temperature.
3. Combine (1) and (2) to determine the volume fraction of crystallization when the mass is held at a given temperature for a given period of time.

This is normally accomplished by using the Johnson-Mehl-Avrami equation and developing $T-T_c$ (time-temperature-transformation) diagrams. Let us consider each of these topics.

3.3.1. The Nucleation Rate

A nucleus is a precursor to a crystal. (A crystal is an assemblage of atoms in a regular, periodic array. In addition, we will now add here that a crystal has recognizable growth habit planes.) A nucleus is also a periodic assemblage of atoms, but it does not have recognizable growth habit