Optical and Photonic Glasses

Lecture 7:

Structures of Glass III and Phase Separation

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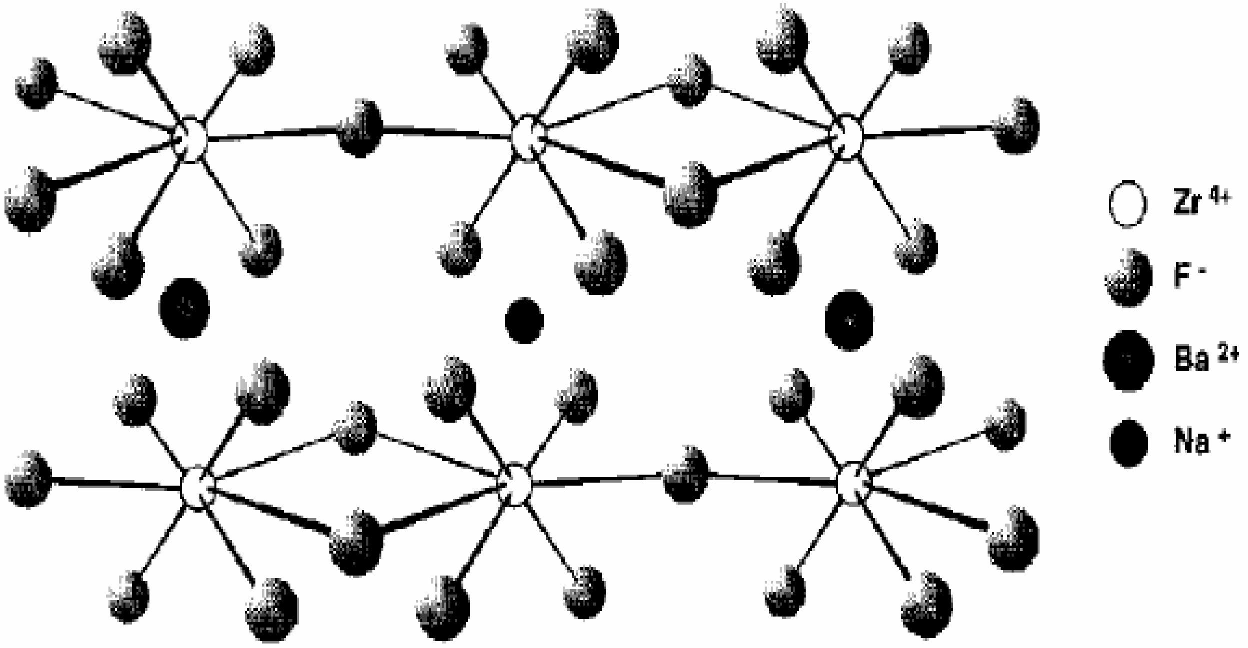
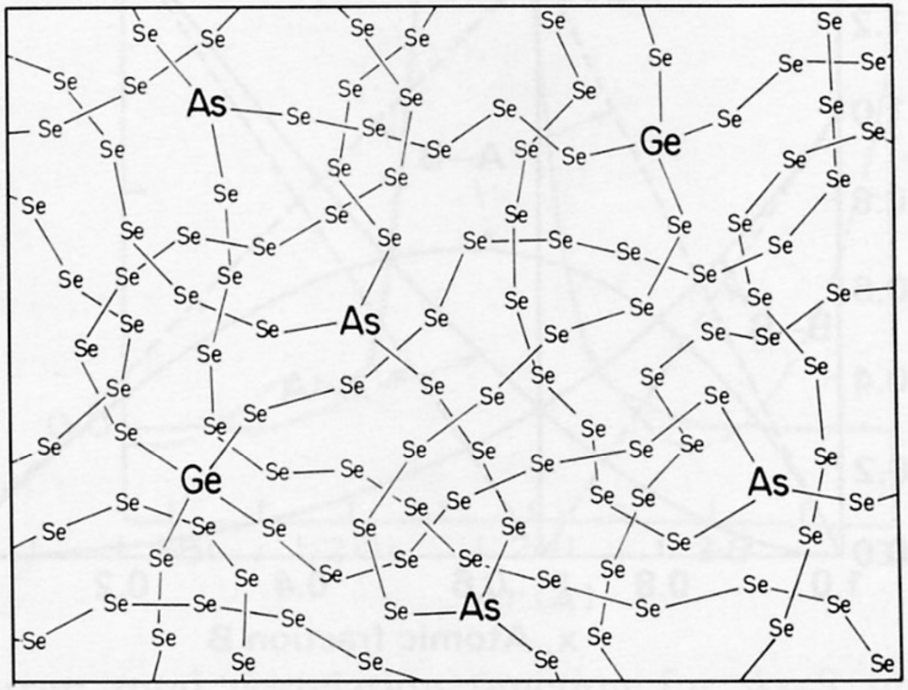
Halide glasses such as the ZrF_4-based ones are more ionic than oxide glasses and the network-forming cation, Zr^{4+}, has higher coordinations than those predicted by Zachariasen's rules (CN_{Zr} has been found to be between ~ 6 - 8).



Chain-like skeleton in the structure of a $ZBLAN_{6.6}$ glass (57.0 ZrF_4-28.1 BaF_2-3.3 LaF_3-5.0 AlF_3-6.6 NaF, in mol%).

(Adapted from: M.C. Goncalves and R.M. Almeida, Mat. Res. Bull. 31 (1996) 573)

Chalcogenide glasses, on the other hand, are more covalent than oxide glasses. The CN_{Se} is 2 (like that of BO species, but with the formation of many Se-Se bonds, unlike in the oxide case) and those of As and Ge are 3 and 4, respectively. The $AsSe_3$ pyramids have a lone electron pair opposite to the Se atoms.



2-D representation of the bonding in Ge–As–Se glass. Note cross-linking of linear chains by As (3-coordination) and Ge (4-coordination). (After R. Zallen, *The Physics of Amorphous Solids*, Fig. 3.7, p. 98. Wiley & Sons, New York, 1983. Reproduced with permission of the publishers.)

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

Free volume in a glass

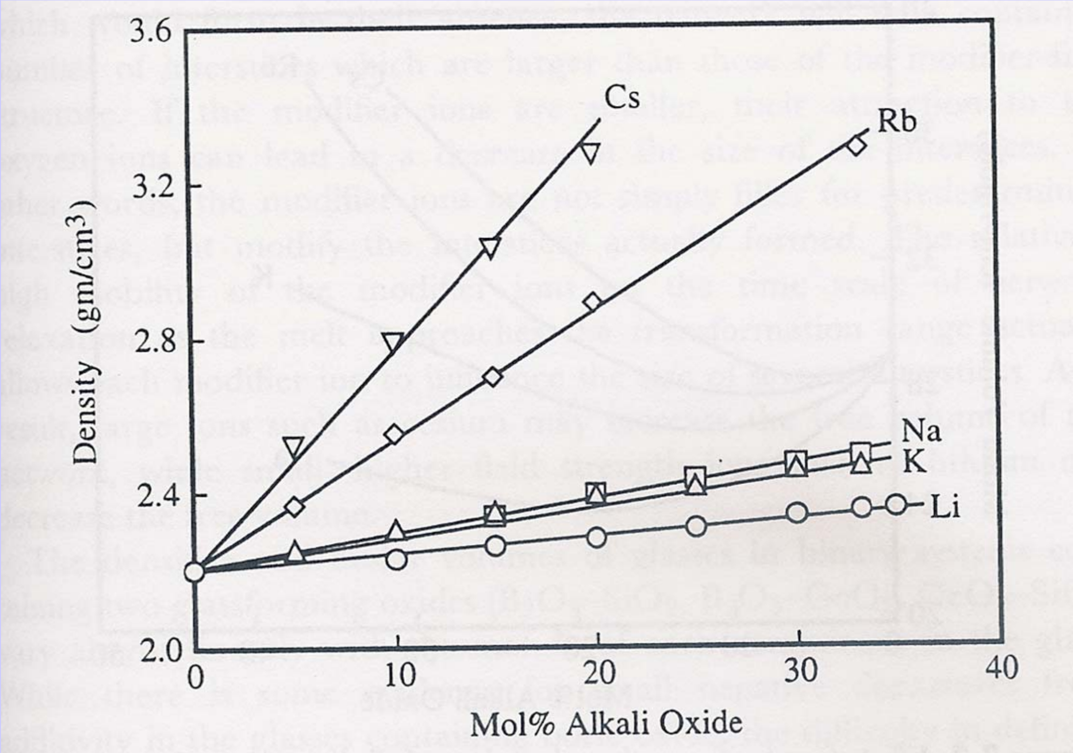
There is a macroscopic structural parameter, designated by free volume, which is closely related to the macroscopic *density*, a basic property of the glass. If the molar volumes ($V = M/\rho$) of the glass and corresponding crystal are designated by V_g and V_x, respectively, the corresponding free volume is given by:

$$V_f = 1 - V_x/V_g$$

The free volume of **v-SiO$_2$** ($\rho = 2.2 \times 10^3$ kg/m^3) with respect to the densest four-coordinated crystalline form of silica, **coesite** ($\rho = 2.9 \times 10^3$ kg/m^3), is 0.24 (or 24%), corresponding to a large fraction of interstitial space, which is "free" for possible accommodation of modifier ions such as Na^+ or Ca^{2+}.

However, if the comparison term is α-quartz ($\rho = 2.65 \times 10^3$ kg/m^3) rather than coesite, the free volume of v-SiO$_2$ will only be 17%.

(Adapted from: *Introduction to glass science and technology*, J.E. Shelby, RSC paperbacks, 1997)

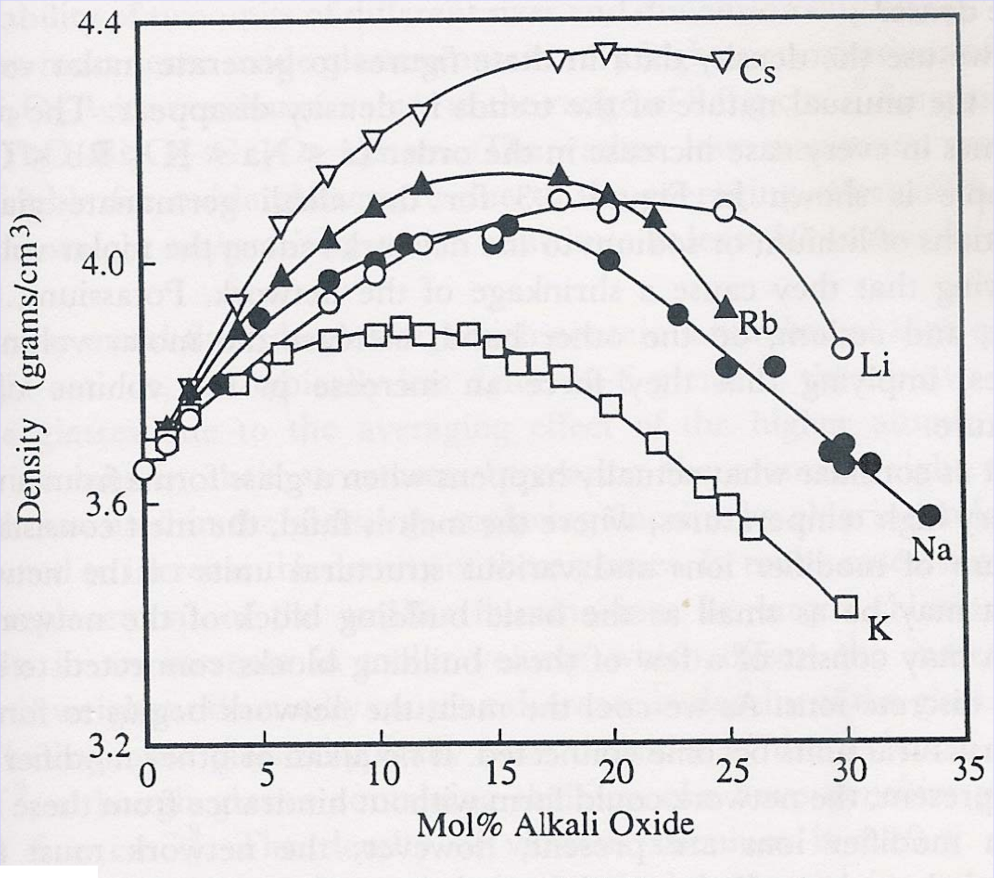


Effect of composition on the density of alkali silicate glasses

The behavior of glass density is not simple.

Although the free volume concept would suggest that a significant amount of modifier ions could be added to silica glass, increasing the mass without a volume increase and, therefore, increasing its density, this figure shows that things are not that simple. In fact, the glasses containing potassium are less dense than those containing sodium, despite the fact that K is almost twice as heavy as Na.

(Adapted from: *Introduction to glass science and technology*, J.E. Shelby, RSC paperbacks, 1997)



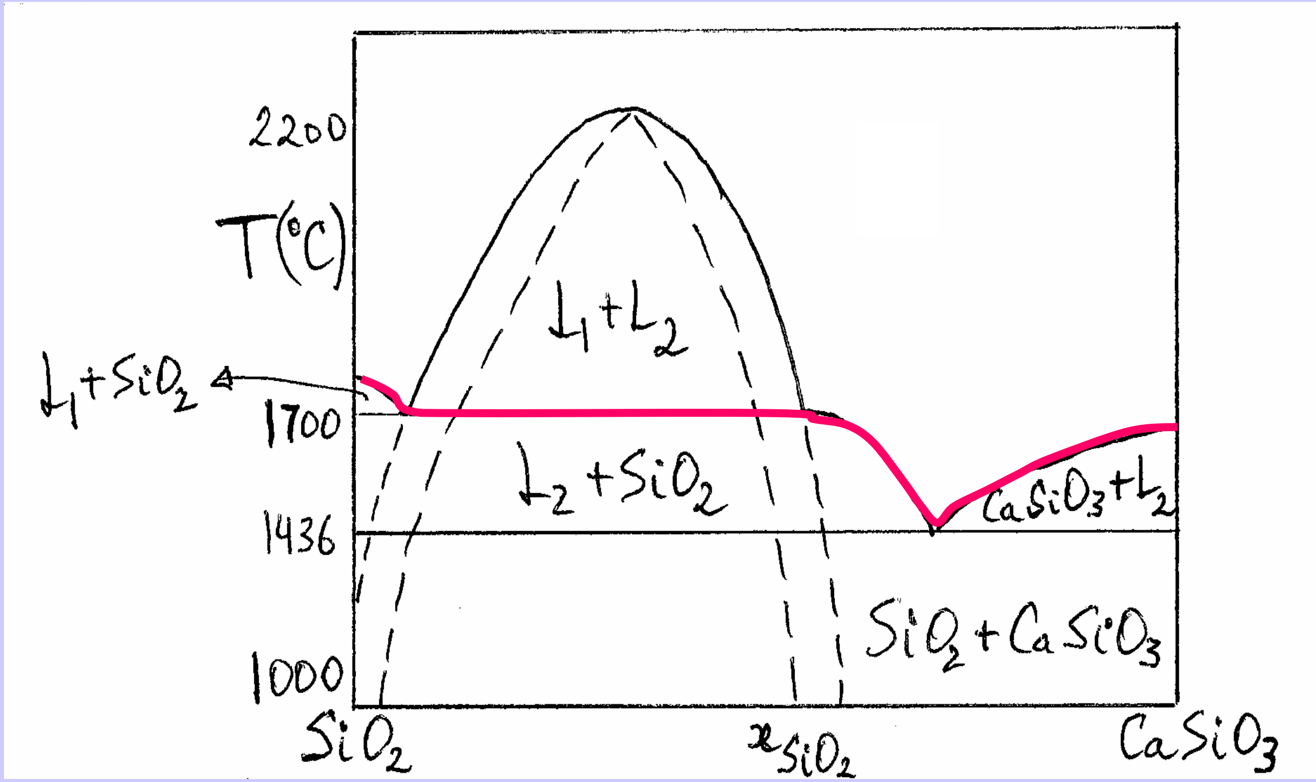
Effect of composition on the density of alkali germanate glasses

The situation is even more complicated in alkali germanate glasses, where not only K-containing glasses are less dense than those containing Na and Li (!), but also the GeO_2-Li_2O glasses with > 20 mol% Li_2O are denser than K-, Na- and Rb-containing glasses. On top of this remarkable behavior, all curves show **maxima** at some intermediate modifier content, a fact known as the *germanate anomaly*.

Phase separation in glass

Several glass-forming systems, including the commercially important **silicates** and **borates**, exhibit, for certain compositions and preparation conditions, the phenomenon of "*glass-in-glass*" phase separation, or immiscibility.

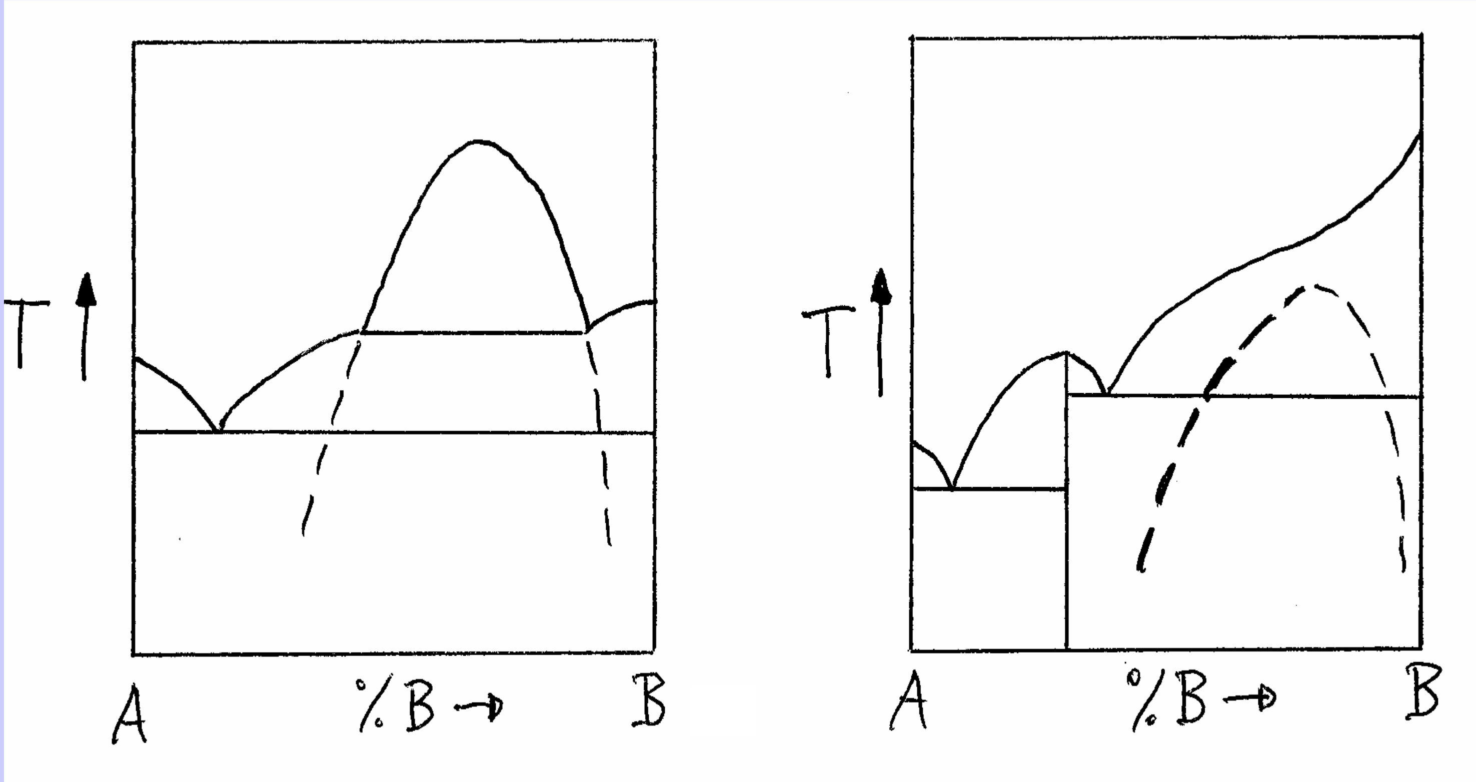
Above the **liquidus** temperature, T_L, this occurs typically in SiO_2-MO systems, with M = Mg, Ca, Sr, Fe, Zn. This is called *stable* immiscibility, because the two liquids (L_1 and L_2) are the stable situation above T_L.



Below T_L, as shown here, it occurs in binary systems such as SiO_2-R_2O (R = Li, Na, K), with *S-shaped* liquidus lines, or as the extension of a stable two-liquid region.

This is called *metastable* immiscibility, because it occurs at lower temperature, when the supercooled liquid is rather viscous and a homogeneous glass may be obtained on cooling from the melt. However, further reheating will lead to phase separation.

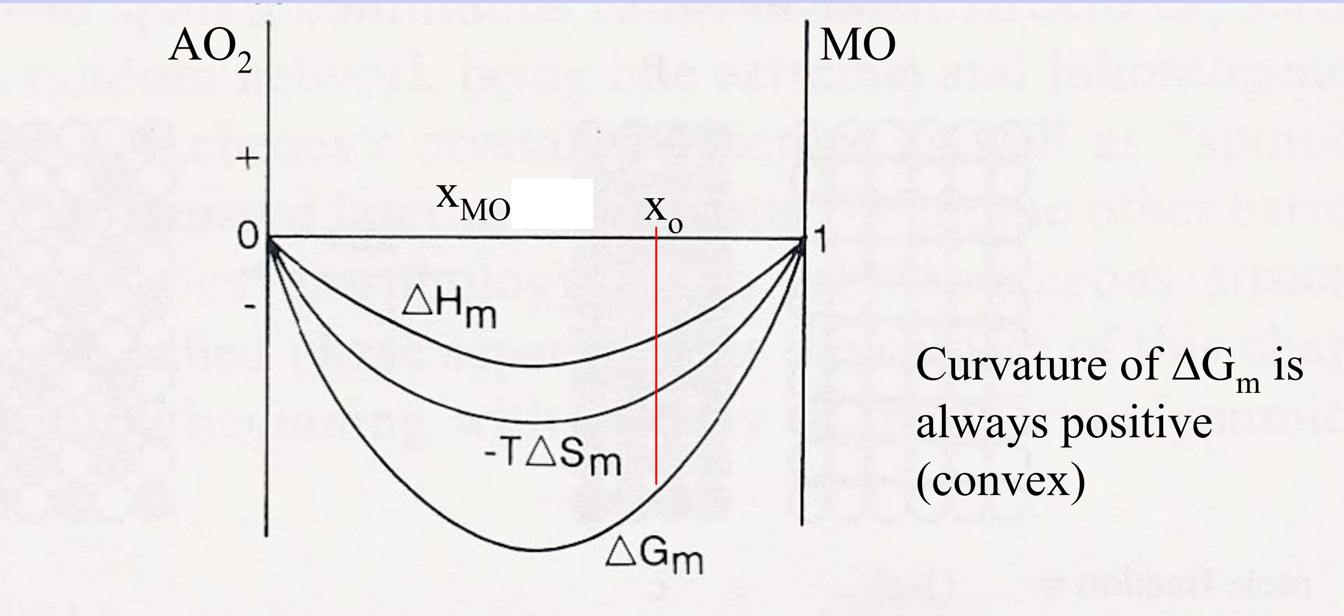
Metastable immiscibility (below liquidus) is the technologically most important type of glass-in-glass phase separation.



For immiscibility to occur, the separation of a liquid into two phases has to lead to a decrease in G. In terms of the **free energy of mixing**, ΔG_m, of the two components of a (1-x) AO_2-x MO binary system (like SiO_2-CaO), one can write:

$$\Delta G_m = \Delta H_m - T\,\Delta S_m = G_{mixture} - x\,G_{MO} - (1-x)\,G_{AO_2}$$

The entropy of mixing, ΔS_m, is always positive. For two liquids (one AO_2-rich and one MO-rich) which are miscible at a given T, ΔH_m is either negative (exothermic mixing) or positive but small, so immiscibility would lead to an increase in ΔG_m, compared to the value for a single, homogeneous phase (with x_o mol% MO) and therefore it does not occur.

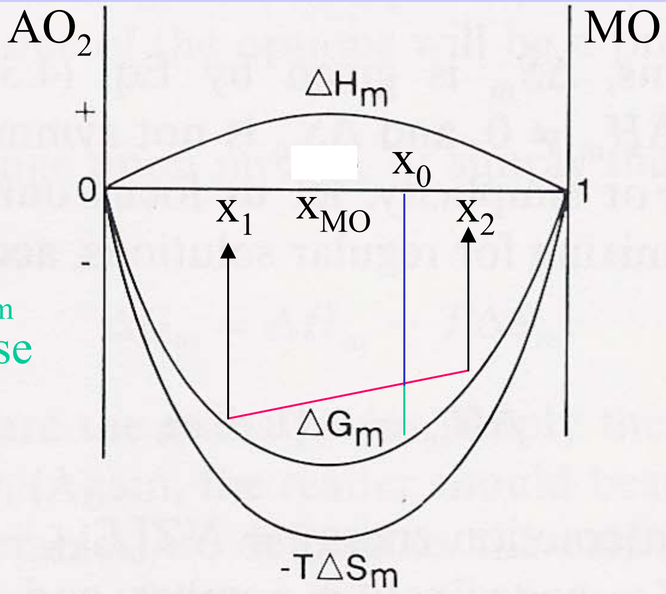


Curvature of ΔG_m is always positive (convex)

Free energy of mixing when the heat of mixing is negative.

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994).

When ΔH_m is positive, but small and the temperature is high enough (above a critical value T_c), any separation of a homogeneous liquid into two separate phases would always lead to an increase in ΔG_m and therefore there is no immiscibility.



Tie line

ΔG_m for the separate phases (x_1 and x_2)

Further decrease in ΔG_m for a homogeneous phase (x_0)

Free energy of mixing when the heat of mixing is positive, but the temperature is high.

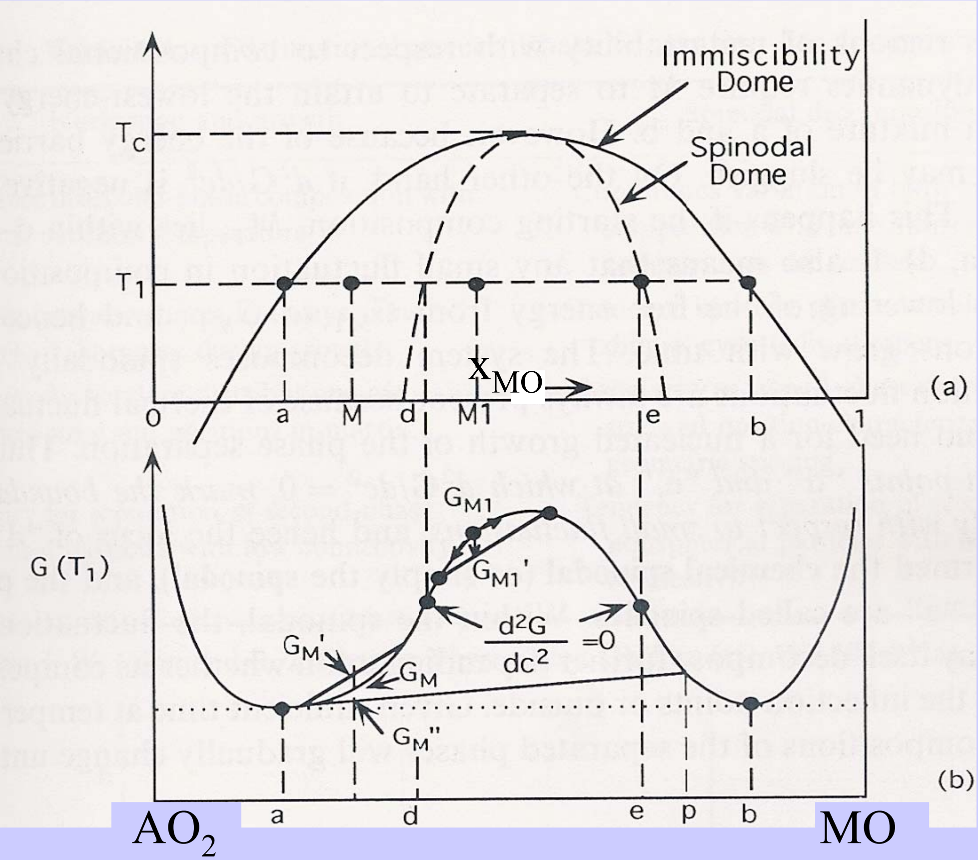
(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994).

For two immiscible liquids, $\Delta H_m >> 0$ and, for a temperature below T_c, like T_1, any initial composition x_M, between **a** and **b**, may lower its ΔG_m by separating into two phases with compositions **a** (AO_2-rich) and **b** (MO-rich), given by the intersection of the horizontal @ T_1 with the *immiscibility dome*, in proportions given by the *lever* rule:

$$x_a / x_b = (x_b - x_M) / (x_M - x_a)$$

This is a consequence of the fact that the ΔG_m curve is no longer convex throughout, but rather changes its curvature at two separate inflection points.

Note: $\Delta G \; \alpha \; (d^2G/dx^2)$



(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994).

Two typical cases, may then be distinguished, depending on whether: (1) the initial composition x_{MO} is between the minimum **a** and the inflection point **d** (e.g. x_{MO}=M, or between **e** and **b**), or (2) between the two inflection points **d** and **e** (e.g. x_{MO}=M1).

In the first case, one has $d^2G/dx^2 > 0$, so small compositional fluctuations lead to an increase of ΔG_m ($G_{M'} > G_M$) and there is no phase separation. Only large enough fluctuations will lead to immiscibility into two phases **a** and **b** (e.g. $G_{M''} < G_M$). The system is said to be metastable against small compositional fluctuations.

In the second case, however, corresponding to the region inside the *spinodal* curve, one has $d^2G/dx^2 < 0$ (downward curvature of ΔG_m) and there is no thermodynamic barrier against immiscibility (always $G_{M1}' < G_{M1}$), no matter how small the compositional fluctuations may be. The system will spontaneously phase separate into two phases **a** and **b**.

The resulting *morphology* will also vary.

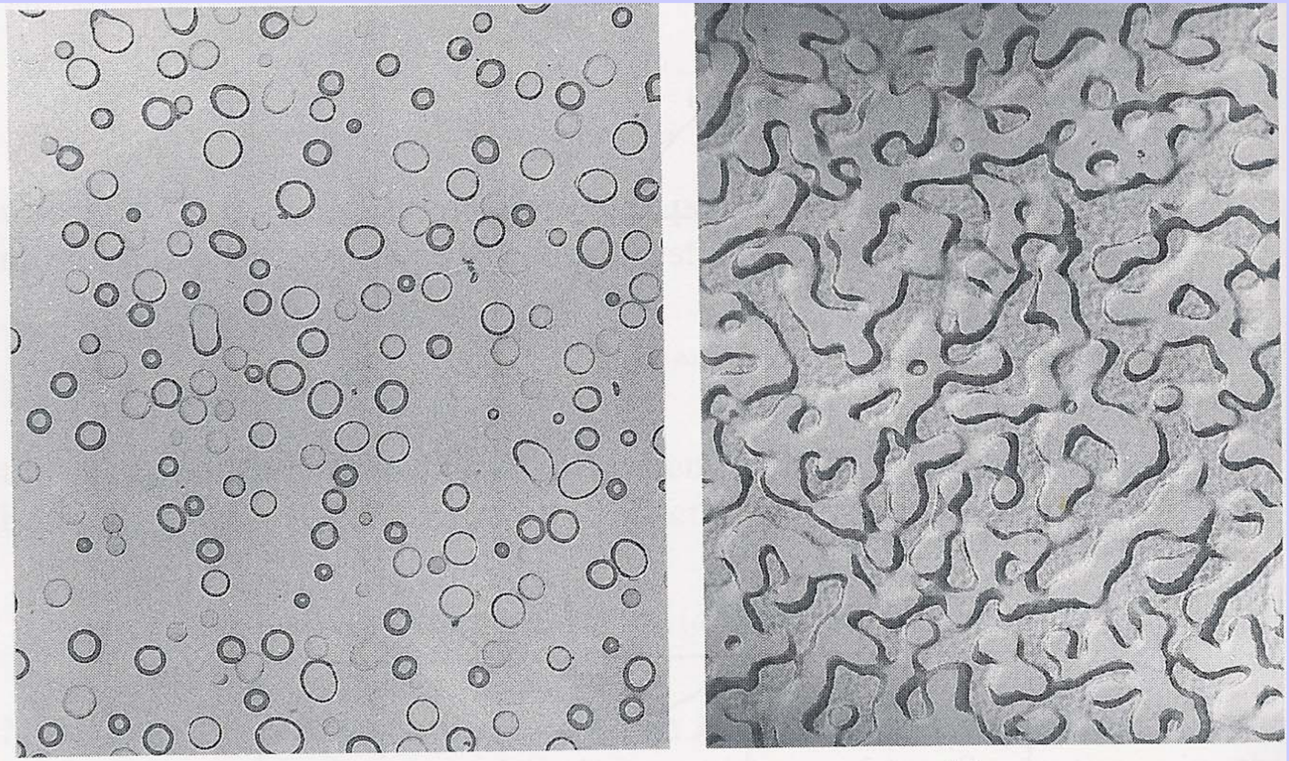
In the first case, for compositions between the immiscibility dome and the spinodal, along the temperature horizontal, the system will only phase separate as a result of compositional fluctuations large enough (large amplitude, but small spatial extent) to cause the formation of *nuclei* of a second phase. So immiscibility occurs by *nucleation* and *growth* of small *droplets* within the glass matrix and it is generally sluggish.

In the second case, for compositions inside the spinodal curve, any homogeneous (scl) melt is unstable relatively to any minor compositional fluctuations and it will spontaneously separate into two phases. These compositional fluctuations have small amplitude, but large spatial extent and the immiscibility develops quickly, into two interconnected phases (like two *spaghettis* of different colors). However, for any temperature T_1 which happens to be below T_L, this immiscibility will still be metastable, in the sense that fast cooling of the melt may actually lead to a homogeneous glass, whereas only further reheating will lead to phase separation.

The two <u>possible morphologies</u>: (a) **droplet**-like (classical phase separation by *nucleation and growth*); (b) **interconnected (***spinodal decomposition).*

Soda-lime silica glass

Vycor glass (before leaching)



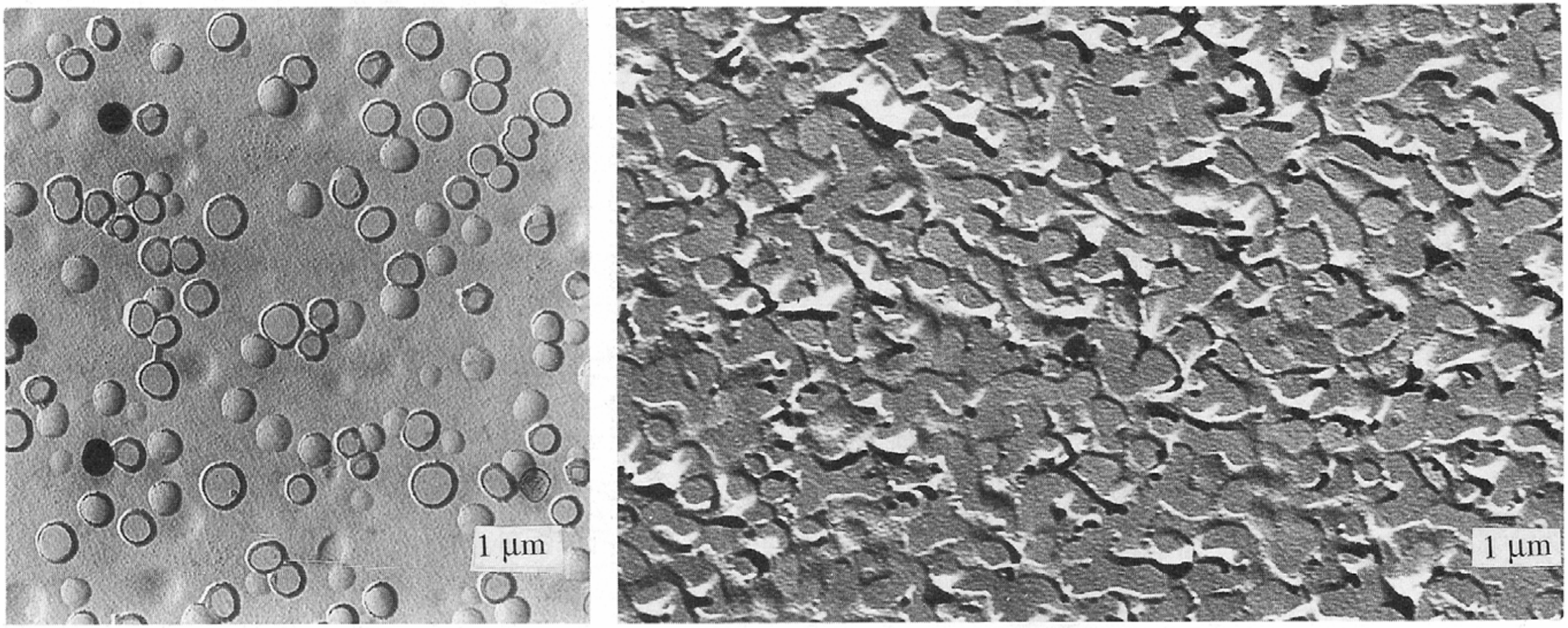
(a) (b)

Microstructure of (a) soda lime silica glass heated at 740°C for 7.25 h (14,000 ×) showing nucleated droplet phase separation; (b) Vycor glass heated at 700°C for 5.5 h (24,000 ×) showing spinodal decomposition. (After H. Rawson, *Properties and Applications of Glass*, Fig. 10. Elsevier Science Publishers, Amsterdam, Netherlands, 1980.) Reproduced with permission of the Publisher. Photographs Courtesy of H. Rawson, University of Sheffield, Sheffield.

(Vycor, a Corning product, is almost pure silica glass, prepared by spinodal decomposition of sodium borosilicate glass).

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994).

Examples of phase separation in a sodium borosilicate glass: (a) droplet-like morphology; (b) interconnected morphology. (Note: *nanoscale phase separation* was discovered fifty years ago by means of TEM; the much *large*r *scale* phase separation shown below is only obtained after **reheating** the **initial glass**).



(a) (b)

(a) Sodium borosilicate glass from the left portion of the immiscibility region in Fig. 4-12b after reheating. Note the nucleated type of phase separation. (After W. Vogel, *Chemistry of Glass*, Fig. 7.21, p. 111. Amer. Ceram. Soc., Columbus, Ohio, 1985.) (b) Sodium borosilicate glass from the center of the immiscibility region in Fig. 4-12b. Note the separation by spinodal decomposition. (After W. Vogel, *Chemistry of Glass*, Fig. 7.22, p. 111. Amer. Ceram. Soc., Columbus, Ohio, 1985. Photograph Courtesy of W. Vogel, Otto Schott Institute, Jena.)

(Adapted from: *Fundamentals of inorganic glases*, A.K. Varshneya, Academic Press, 1994).