Module 6 – Glass Transition and Glass Stability

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Introduction

Given the need for significant thermal processing of glass throughout preform development and fiber drawing, the impact of such processing on glass structure, stability, and ultimately, mechanical, optical and chemical properties, is of great importance. The present module seeks to provide an introduction to the rich range of phenomena and concepts critical to an understanding of the glassy state and its response to thermal treatment. We will see that both thermodynamic driving forces and kinetic factors play significant roles in this response and that they help to inform the development of appropriate processing conditions for the development of all technical glasses, including optical fibers. The student is referred to supplementary reading (see end of module) for more in-depth discussion of these issues.

6.1 The Glass Transition

Figure 6.1 depicts a generalized plot of volume vs. temperature for a good glass forming material (i.e. no tendency for crystallization under the cooling rates used). In view of the inverse relationship between volume and density, such a plot also provides insight into the influence of cooling rate on the density (and, to first order, the refractive index) of the glass as it is cooled from the melt.

The discussion below assumes that the material is cooled beginning in it liquid state from a temperature greater than the melting point of the corresponding crystal T_m. Below the thermodynamic melting point of the material and the temperature at which it enters the "glass transformation range" indicated on the diagram, the material is termed a supercooled liquid. By

this, it is meant that the material is below its expected crystallization temperature and yet it still is characterized by a structure consistent with that of the liquid. As the supercooled liquid is cooled within this temperature range, structural rearrangements can occur with a speed sufficient to follow the experimental cooling rate and to attain the characteristic volume anticipated through an extension of the liquid phase line at each temperature. The thermal expansion coefficient observed in this supercooled liquid range, therefore, is consistent with that of the liquid.
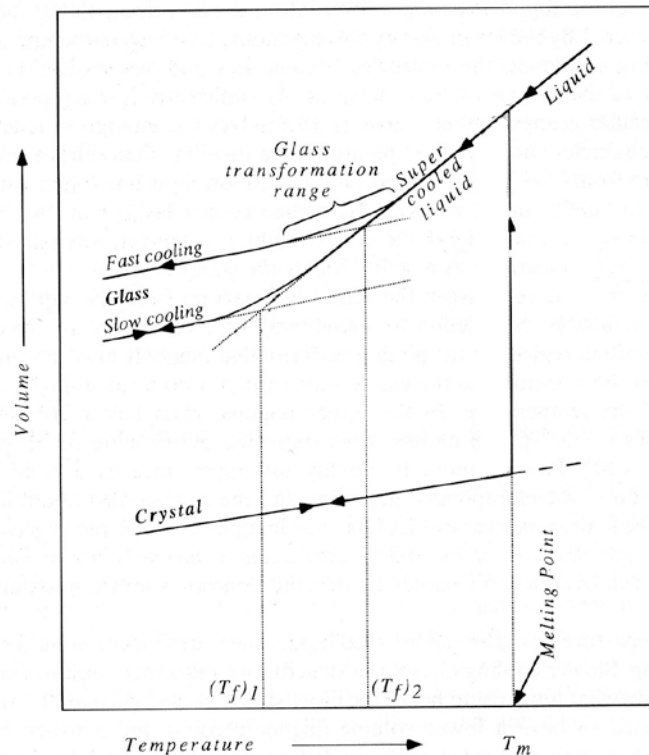

Figure 6.1. *(Adapted from Varshneya; Figure 2.1 page 15)*

However, upon cooling to within the glass transformation range, an increasing number of molecular units comprising the material cannot rearrange within a time scale necessary to respond to the imposed cooling rate. This is reflected in an increased viscosity as the temperature is reduced with the viscosity generally increasing from 10^8 to 10^{12} Pa-s through the transformation range. If the material is considered to consist of a distribution of structural components with a range of relaxation times (characteristic rearrangement times needed to respond to a given temperature change), then the glass transition range corresponds to a gradual "freezing" in of structures possessing shorter and shorter relaxation times eventually resulting a final glass structure (corresponding to a specific volume or density) that is ultimately related to the cooling rate used. A faster cooling rate will result in the more rapid loss of longer range structural rearrangement at higher temperatures, producing a lower density structure. Thus, the nature of the glass formation process and the glass structure formed can be described in terms of the relative magnitudes of the intrinsic relaxation rates characteristic of the primary molecular units of the glass and the experimentally imposed cooling rate.

The correspondence between the experimentally imposed cooling rate and the structural density produced upon glass formation can be quantified in terms of a fictive temperature (T_f). This parameter is a function of the cooling rate (see Figure) and it provides a means to describe the glass structure formed as corresponding to that of a supercooled liquid equilibrated at the temperature, T_f. Essentially, T_f can be thought of as the temperature at which the supercooled liquid structure is frozen-in as the material moves through the transformation range to the glassy state.

It is important to note that the glassy state is unstable with respect to the equilibrium liquid state and that, with sufficient thermal energy, the glass structure will continue to relax toward configurations consistent with the liquid as the kinetic restrictions on molecular rearrangement are lifted. This results in deviations from the cooling curve upon reheating that reflect the varied thermal paths taken by the glass through the transformation range.

This sensitivity of glass structure and the associated physical properties, e.g. density, thermal expansion coefficient, viscosity, to thermal history can result in a variety of effects important to the formation of optical fibers. For example, since refractive index can be shown to scale with density for a given glass composition, variation in index from that of a bulk glass piece can be observed in glass subjected to the rapid cooling rates typical of standard fiber drawing.

In bulk glass pieces (e.g. melt-derived performs), the variation in cooling rates obtained between the surface and the interior of the glass body results in a distribution of local glass density values (and associated optical properties) across the cross-section of the piece. Such variations in structure will give rise to a built-in stress distribution within the glass, requiring that such glass pieces be annealed by reheating and holding at temperatures near the glass transformation range. This process provides the added time-at-temperature to allow structural relaxation to more completely homogenize the glass density throughout the volume and reduce residual stress in the glass piece. Conversely, the effect of heterogeneous cooling rates in plate glass is often used to create an engineered compressive surface stress on the glass, thus increasing its resistance to brittle failure (thermally tempered glass).

6.2 Glass Stability

Glass formation can be described in terms of a kinetically limited process that impedes the thermodynamically expected crystallization of the liquid phase upon cooling. This approach is often termed the "kinetic theory" of glass formation. In this context, it is the externally imposed cooling rate, with respect to the intrinsic relaxation rate of structural constituents in the material and the rate of nucleation and growth of a crystalline phase, that determines the potential for glass formation. Such cooling rates are readily attained in the laboratory (and manufacturing) frame for silica and many silicate and other metal oxide-based glass forming systems. This was the assumption used in discussions in the previous section. However, some compositions and, indeed, many non-oxide glass systems introduced in the undergraduate Module 1 (e.g. fluorides, chalcogenides), exhibit structures characterized by much more rapid relaxation rates in the molten state thus often requiring faster cooling rates to insure glass formation. In addition to the influence on crystallization phenomena, the effect of these relatively fast relaxation rates is also observed in the more sensitive dependence of glass viscosity on temperature about the glass

transition range. A more rapid modification in glass viscosity with temperature presents significant engineering challenges with regard to temperature control during processing to avoid unintended increases (solidification) or decreases (melting) of the glass during fiber preform formation or drawing. Examination of glass viscosity and its correlation with key structural kinetics and thermodynamics in glass forming systems still present fertile ground for fundamental and applied research and has resulted in the development of terminology (i.e. "fragile" and "strong" glasses) that serves to categorize glasses according their viscosity behavior with temperature about the glass transition range [C.A. Angell, J. Non-crystal. Sol. 102, 205 (1988).].

In "fragile" glasses (those exhibiting a more rapid variation in viscosity with temperature about Tg) avoiding thermodynamically favored crystallization processes during glass formation and during the subsequent re-heating of the glass needed for preform development and fiberization requires that more rapid heating and cooling rates be used to maintain the glassy structure and avoid the nucleation and growth of a crystalline phase. Such a phase transformation, if allowed to occur, would produce crystalline inclusions that would serve as optical scattering centers and significantly impact the chemical and physical characteristics (e.g. strength) of a resulting fiber.

Glass stability, characterized by a resistance to nucleation and crystallization from the glass host, has been the focus of decades of research motivated both from the standpoint of deleterious effects on optical fiber formation and in terms of the creation of technologically important crystal-glass nanocomposite materials and polycrystalline ceramics (glass-ceramics). Early insight into the contributions of thermodynamic and kinetic factors to the nucleation of a second, crystalline phase can be developed through the principles of classical nucleation theory, introduced below. The interested reader is referred to numerous texts and reviews containing higher level discussions of nucleation and crystallization theory.

6.2.1 Nucleation

The present discussion is limited to nucleation from the liquid phase without the influence of an interface (i.e. homogeneous nucleation). Moreover, the composition of the precipitating crystalline phase is assumed to be the same as that of the liquid. While heterogeneous nucleation (i.e. initiation of the phase transformation at an interface, surface or third-phase inclusion) will be more likely under the conditions of interest to optical fiber development, homogeneous nucleation will suffice to introduce the key aspects of the process. The treatment can be readily extended to include heterogeneous effects through the characteristic energy terms associated with the interface.

The free energy change accompanying the formation of a nucleus of a second material phase within the host (in this, case, a crystalline phase domain within an amorphous, glass matrix), includes energies contributions associated with the bulk (volume) free energy of crystallization and the development of a new interface between the newly formed crystal nucleus and the liquid (glass).

$$\Delta G_T = \Delta G_S + \Delta G_V$$

$where: \ \Delta G_T = total \ free \ energy \ change; \ \Delta G_{S(V)} = surface \ (volume) \ free \ energy \ change$

(Equation 6.1)

The change in volume free energy is negative (energy release) while a positive energy change is associated with the development of the higher energy interfacial structure separating the two material phases (i.e. the crystalline lattice of the nucleus and the amorphous structure of the surrounding glass).

For a spherical nucleus,

$$\Delta G_S = 4\pi r^2 \gamma$$

(Equation 6.2)

$$\Delta G_V = \frac{4}{3}\pi r^3 \Delta G_\upsilon$$

(Equation 6.3)

where:

ΔG_υ = volume free energy change / unit volume and has a negative value at temperatures below the thermodynamic melting point for the associated crystal

γ = interfacial energy
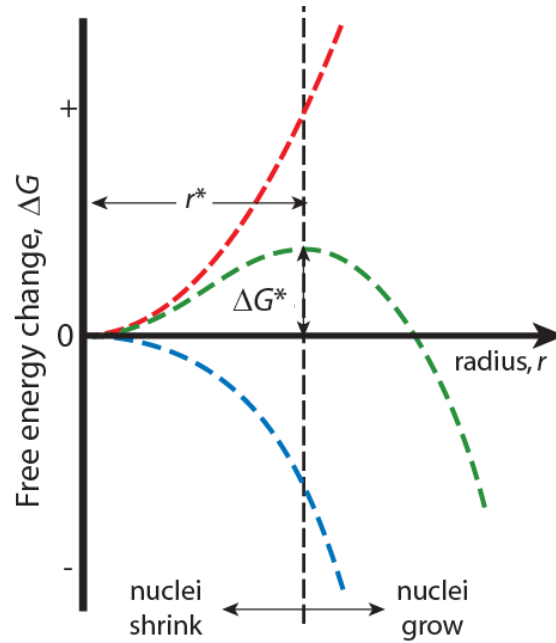
r = nucleus radius.

Figure 6.2

Thus, the two primary contributions to the total free energy change for nucleation scale differently with the nucleus radius. **Figure 6.2** contains a generalized plot of the two energy components and the total free energy change as a function of nucleus radius.

Note that the opposing trends of the energy components with radius results in a net free energy change function that reaches a maximum at some radius value. This "critical" radius, r*, defines the nucleus size beyond which further nucleus growth actually decreases the free energy of the system; these nuclei are considered "stable". Using calculus, the position of this maximum in the free energy can be found:

$$r^* = \frac{-2\gamma}{\Delta G_v}$$

(Equation 6.4)

The corresponding total free energy associated with the critical nucleus radius is then given by:

$$\Delta G_T^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$$

(Equation 6.5)

and corresponds to the activation energy barrier for the formation of a stable nucleus.

Nuclei smaller than the critical radius decrease the system free energy by shrinking and are termed "unstable". Clearly, the critical radius value will be dependent upon the precise functional dependence of the interfacial energy and volume free energy change terms in the

equations above. Inherent in the current treatment of the stability of glass under temperature change is interest, then, in the temperature dependence of the two energy terms.
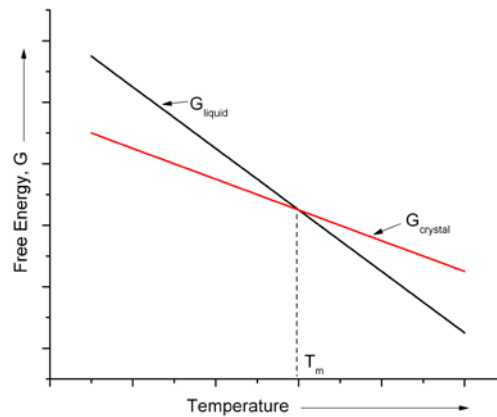

Figure 6.3

The interfacial energy is assumed largely temperature insensitive in the temperature range near the melting temperature. The functional form of the $\Box G \Box$ term, however, can be approximated as being linear with temperature near the melting point as follows.

The free energy for the liquid and crystal phases can be written as:

$$G_L = H_L - TS_L$$
$$G_C = H_C - TS_C$$

(Equation 6.6)

where: $G_{L,C}$, $H_{L,C}$ and $S_{L,C}$ are the free energy, enthalpy and entropy of the liquid (L) and crystal (C) phases, respectively.

It is assumed that the enthalpy and entropy terms are independent of temperature near the melting point. Moreover, it is remembered that, at the melting point, the free energies of the liquid and crystalline phases are equal (i.e. $G_L = G_C$ at T_m).

Figure 6.3 provides a graphical representation of these free energy terms near the melting point, T_m.

With the above assumptions,

$$\frac{dG_L}{dT} = S_L$$

<div align="right">(Equation 6.7)</div>

$$\frac{dG_C}{dT} = S_C$$

and integrating from T to Tm:

$$G_L(T_m) - G_L(T) = S_L(T_m - T)$$
$$G_C(T_m) - G_C(T) = S_C(T_m - T)$$

<div align="right">(Equation 6.8)</div>

and finding the free energy change associated with the formation of the crystal phase (i.e. the free energy change with crystallization, $\Box G_x$, by subtraction of the above expressions:

$$G_C(T) - G_L(T) = \Delta G_X = \Delta S_X(T_m - T)$$
$$where: \quad -\Delta S_X = S_L - S_C = \Delta S_f \ (entropy \ of \ fusion)$$

<div align="right">(Equation 6.9)</div>

Tm – T, in the present context is positive (i.e. T < Tm) and is often called the "undercooling". The $\Box S_x$ term is negative in this temperature range, making the free energy change associated with crystallization negative.

Recognizing that:

$$\Delta G = 0 \ at \ T_m$$
$$then$$
$$\Delta S_f = \Delta H_f / T_m$$

<div align="right">(Equation 6.10)</div>

And substituting into **Equation 6.9**:

$$\Delta G_x = \Delta T \cdot \Delta H_f / T_m$$

<div align="right">(Equation 6.11)</div>

where, in this case, $\Box T = T - T_m$ making the term negative for the undercooled liquid.

In the context of the previous discussion of energetic factors contributing to critical nucleus radius:

$$\Delta G_v = \Delta G_x$$

<div align="right">(Equation 6.12)</div>

The volume free energy associated with the formation of a critical nucleus is therefore found to scale with the degree of undercooling through the volume free energy change upon crystallization (see **Equation 6.5, 6.11, 6.12**).

As described earlier, the glass stability generally refers to the resistance of the glass to nucleation and crystallization. Further, it is the rate of nucleation and growth of the resulting nuclei that will be a key factor in determining whether elevated temperature processing of glass for preform development or fiber drawing will be sufficiently limited (short time at temperature) to avoid nucleation and the formation of a material phase with a deleterious impact to the fiber optical and mechanical properties.

The energetics of the nucleation process described above, provide insight into the overall rate of nucleation. In an undercooled liquid (melt), random fluctuations in local structure are anticipated, driven by the thermal energy of the system. With time, the system "samples" various, often transient, molecular configurations until the lower energy, crystalline structure is formed. If there was not barrier to the formation of a stable nucleus (i.e. no contribution from the surface free energy in the formation of a nucleus), then the nucleation rate (I) could be approximated by the vibrational frequency of the atoms, $\square$, (i.e. the rate at which atoms could collide together to form the new structure) multiplied by, n, the number of atoms in the system (I = n$\square$).

Based on our earlier discussion, however, successful stabilization and growth of this structure will only occur if it is larger than the critical radius. In a qualitative sense, the probability that a stable nucleus will form during this initial period of random thermal motion will increase as the size of the critical nucleus decreases. Taken another way, the time necessary to form the critical nucleus will decrease as r* decreases, i.e. the "nucleation rate" will increase. Thus, the energy associated with the formation of a stable, critical nucleus **Equation 6.5**) represents a "thermodynamic" barrier to the nucleation process and influences the rate at which stable nuclei are formed.

Based on the energetic arguments just described, the nucleation rate should increase, unbounded, as the melt temperature is reduced (and the degree of undercooling is increased). This would imply an inherently unstable amorphous system at room temperature that is clearly not the case for most technologically important glass systems, included those used for optical fiber telecommunication systems. Referring back to the last section and to Module 1 (undergrad), the dynamics of the glassy material are also significantly impacted by a reduction in temperature, typically showing multi-order-of-magnitude changes in viscosity. Thus, despite thermodynamic arguments that show a dramatic reduction in critical nucleus radius with decreased temperature, these effects are mediated, and eventually overcome, by the reduced opportunity for atomic diffusion and structural rearrangement that is required to move atoms across the liquid-crystal interface and produce the crystalline structure.

The nucleation process, therefore, is limited by two energetic factors. The first, described in detail above for homogeneous nucleation, is a thermodynamic barrier associated with the need to attain a critical nucleus radius. The corresponding energy barrier can be found in **Equation 6.5**.

The second is often termed a "kinetic" barrier and is associated with the energy to transport (or diffuse) atoms across the interface between the nucleus and the surrounding liquid.

The two energy contributions result in an overall reduction in the probability for stable nucleus formation with time, or a decrease in the nucleation rate, I:

$$I = n\upsilon_o \exp\left(-\frac{\Delta G_\upsilon^*}{kT}\right)\exp\left(-\frac{Q_D}{kT}\right)$$

(Equation 6.13)

where: k = Boltzman's constant, Q_D = activation energy for diffusion (assumed temperature independent), and $\square_o$ = the frequency of vibration for the atom (typically on the order of 10^{13} Hz)

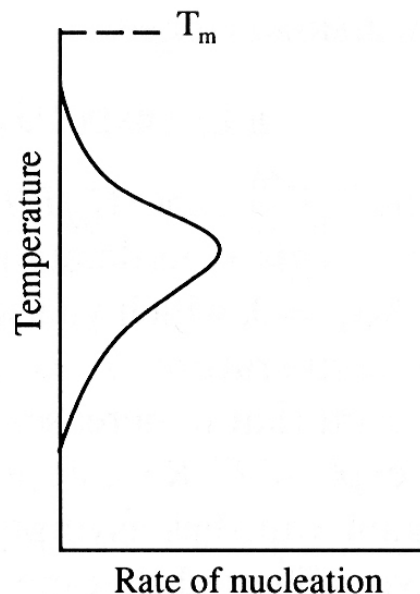The rate, I, is expressed as the number of nuclei formed per unit volume per unit time.

Figure 6.4. *(From Varshneya, Figure 3.9, page 49)*

Again, because the volume free energy change associated with crystallization is temperature dependent (see **Equation 6.11**, the energy barrier associated with the formation of a stable nucleus (in the first exponential term of **Equation 6.13**) is, itself temperature dependent. This makes the nucleation rate, I(T), also temperature dependent.

Figure 6.4 shows the general variation of nucleation rate, I, with temperature. Note that the rate only becomes significant when the undercooling becomes large enough and the volume free energy released upon crystallization (**Equation 6.5** is increased sufficiently to offset the surface free energy produced upon nucleus formation **Equation 6.3**).   Note also that there is a maximum in the nucleation rate at some intermediate degree of undercooling that represents the point at

which the decreasing kinetics of structural rearrangement become the primary rate limiting process in the formation of stable nuclei with reduced temperature.

6.2.2 Crystal Growth

With the successful formation of a population of stable nuclei, the subsequent growth of larger crystals is possible. The growth process can be described in terms of the deposition of atomic layers to the existing nucleus surface, resulting in the advancement of that interface into the liquid (glass melt) and the increase in size of the crystal. Thus, growth will be dependent upon the movement of atoms to the interface (longer range diffusional motion) and their incorporation into the growing structure. The rate of growth, then will depend upon the probability for a successful movement (or "jump" from of an atom from its position on the liquid side of the crystal surface into a position within the crystalline structure (at the interface).

Figure 6.5 depicts the energy landscape associated with this change in atom position and assuming that the system is in an undercooled condition (i.e. $T < T_m$). The difference in free energy between the two minima (for an atom in the liquid state and the atom in the crystalline state) is, as anticipated, the free energy of crystallization, ΔG_x. The activation energy (ΔE) separating the two minima is then related to the energy required to move the atom between these locations.
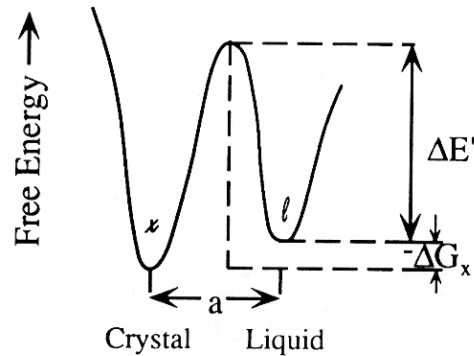

Figure 6.5. *(From Varshneya, Figure 3.10, page 49).*

With this framework, the probability for a successful jump of an atom in either the crystal-to-liquid or liquid-to-crystal direction can be estimated by the jump frequency, υ:

$$\upsilon_{liquid-to-crystal} = \upsilon_o \exp\left(-\frac{\Delta E}{kT}\right)$$

$$\upsilon_{crystal-to-liquid} = \upsilon_o \exp\left(-\frac{(\Delta E - \Delta G_x)}{kT}\right)$$

(Equation 6.14)

where: υ_o = the frequency of vibration for the atom.

Again, it is important to note that, for conditions of undercooling, ΔG_x is < 0, resulting in a larger total energy term in the crystal-to-liquid jump frequency expression and a correspondingly lower jump frequency when compared to the liquid-to-crystal frequency value. Thus, for undercooled conditions, the net rate of successful jumps is from the liquid to the crystalline form, resulting in a net growth of the crystal with time.

A net rate of crystal growth (u) can be obtained by assuming that the interatomic separation (a) in the crystal provides the length scale for advancement of the crystal surface with the addition of each layer of new atoms.

$$u = a(\upsilon_{liquid-crystal} - \upsilon_{crystal-liquid}) = a\upsilon_o \exp\left(-\frac{\Delta E}{kT}\right)\left[1 - \exp\left(\frac{\Delta G_x}{kT}\right)\right]$$

(Equation 6.15)

In a similar manner to the nucleation rate equation (**Equation 6.13**), both a thermodynamic energy term (ΔG_x) and kinetic barrier (ΔE) contribute to the temperature dependence of the growth rate. Variants of this expression can be produced depending upon the mechanistic interpretation of the activation energy ΔE. If the activation barrier is mainly associated with diffusive flow of atoms, the corresponding diffusion coefficient can be written as:

$$D = a^2 \upsilon_o \exp\left(-\frac{\Delta E}{kT}\right)$$

(Equation 6.16)

and the corresponding crystal growth rate is:

$$u = \left(\frac{D}{a}\right)\left(1 - \exp\left(\frac{\Delta H_f \cdot \Delta T}{kTT_m}\right)\right)$$

(Equation 6.17)

where **Equation 6.11** has been used to replace ΔG_x.

Using the Stokes-Einstein expression to relate the diffusion coefficient to the viscosity of the system, the crystal growth rate can be cast in terms of the glass viscosity (η):

$$u = \left(\frac{fkT}{3\pi a^2 \eta}\right)\left(1 - \exp\left(\frac{\Delta H_f \cdot \Delta T}{kTT_m}\right)\right)$$

(Equation 6.18)

where: f = fractional surface area available for growth.

Equation 6.18 thus, explicitly includes an important processing and forming-related material parameter, the viscosity. In this case, the temperature dependence of the growth rate is influenced both explicitly by the undercooling parameter in the exponential term as well as implicitly within the viscosity term. Clearly, as the viscosity increases (e.g. with decreasing temperature), the growth rate decreases, consistent with a decreased rate of structural rearrangement.

Similar to the nucleation rate treatment, it can be seen that the decreasing thermodynamic energy term with decreasing temperature (i.e. $\Box G_k$) serves to increase the crystal growth rate while the activation energy term (associated with diffusional motion and structural rearrangement) eventually offsets the effect of the thermodynamics to reduce and eventually shutdown growth rate as the temperature continues to decrease.
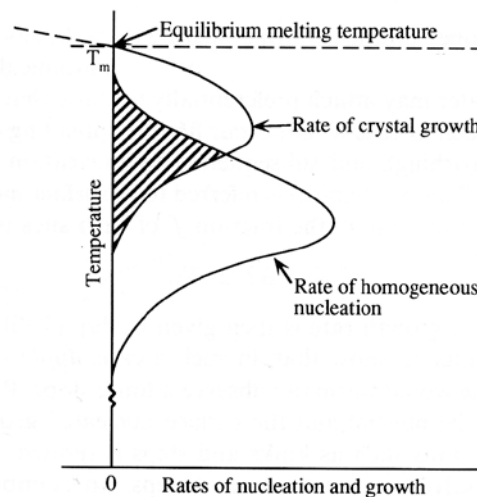

Figure 6.6. *(From Varshneya, Figure 3.13, page 53).*

This effect can be seen in **Figure 6.6** which depicts generalized nucleation and growth rate curves as a function of temperature.

In this case, it is important to note that, dependent upon the specifics of the system involved, the temperature ranges corresponding to high crystal growth and high nucleation rates need not be the same. However, since nucleation must precede growth for the conversion of the glass to its crystalline form, the degree to which the nucleation and growth curves overlap provides insight into the ease with which crystallization can occur in a particular system. For example, a high degree of overlap indicates a broad temperature range over which thermodynamic and kinetic conditions are optimal for both processes. Thus, nuclei that form will grow rapidly. With minimal overlap between the nucleation and growth rate curves, it is possible to process glass in a temperature range with a high crystal growth rate without crystallization. In this case, since limited (or no) nucleation is observed, there will be no nuclei available to sustain growth and thus no conversion of glass to crystal.

In a related context, the multiple temperature thermal treatment schedules can be used to control the size and number of crystals that form in such systems, providing the opportunity to engineer

the microstructure of the resulting "glass-ceramics" to tailor thermal, mechanical, and optical properties for a variety of technological applications.

6.2.3 Nucleation + Growth: Crystallization

Based on the above discussion, a quantitative measure of the crystallization in a given system must necessarily involve the combined effects of nucleation and growth rates with temperature. The Johnson-Mehl-Avrami equation [Johnson and Mehl, Trans. AIMME 135, 416 (1939); Avrami, J. Chem. Phys. 7, 1103 (1939)] effective combines these two rates into an expression for the relative fraction of glass converted to crystal as a function of time.

$$X = \frac{V_x}{V_o} = 1 - \exp\left(-\frac{\pi I u^3 t^4}{3}\right)$$

where: X = volume fraction of crystal phase formed, V_x = volume of crystal phase, V_o = initial volume of uncrystallized material, t = time.
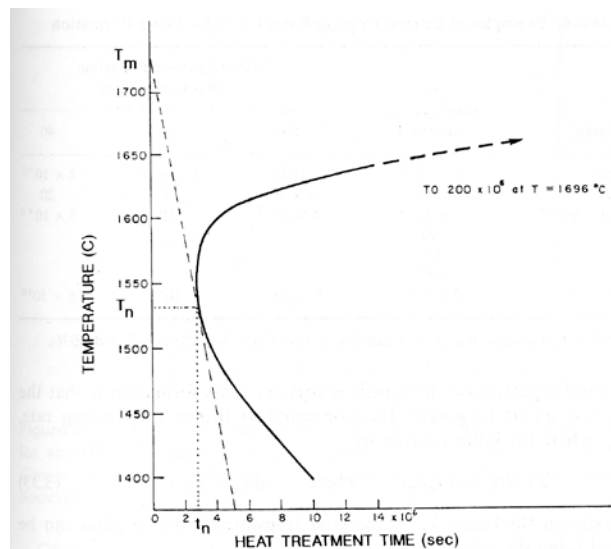

Figure 3-15. Time–temperature–transformation diagram for silica corresponding to a volume fraction crystallized of 10^{-6}. (After D. Uhlmann, *J. Non-cryst. Sol.* 7, 337 (1972). Reproduced with permission of Elsevier Science Publishers.)

Figure 6.7. *(From Varshneya, Figure 3.15, page 55 (NOTE: origin attributed to Uhlmann, see caption).*

With the temperature dependence of I and u developed above, it is possible to plot the transformed fraction of material as a function of both time and temperature. The resulting plot is often referred to as a time-temperature-transformation (TTT) diagram [Uhlmann, J. Am. Ceram. Soc. 66, 95 (1983)]. Such a diagram for silica is shown in **Figure 6.7**.
The curve corresponds to a point at which a volume fraction of 10-6 has crystallized. To the left of the curve, no crystallization has occurred, to the right, the amount of crystallized material is higher than the 10-6 value. Thus, some diagrams would include addition lines of constant transformed fraction at higher values. Note that as the temperature approaches the melting

temperature for the crystal phase (Tm), the time required for transformation becomes infinite since there is no driving force for crystallization (i.e. $\Delta G_x = 0$ at $T = T_m$).

The behavior depicted in the Figure is obtained under isothermal heat treatment conditions. Such a diagram would enable the selection of thermal hold times at a given temperature to provide the degree of crystallization required for a given application. Conversely, a glassy material would be maintained if it can be cooled from the melt at a fast enough rate to avoid crossing the line in the TTT diagram. In other words, the time-temperature trajectory on the TTT diagram must stay to the left of the "nose" of curve. The "critical cooling rate" is then defined as the cooling schedule that is equivalent to the rate given by line beginning at the initial melt temperature and running tangent to the nose. A typical critical cooling rate for silica glass (under homogeneous nucleation conditions) is approximately 10^{-5} C/s while a lower viscosity (lower glass transition range) glass composition, $Na_2O\text{-}2SiO_2$ exhibits a much faster critical cooling rate of 6 x 10^{-3} C/s. Normal air cooling techniques, with cooling rates approaching 10 C/s, easily achieve such rates, making glass formation in such systems readily accessible. For comparison, water has a critical cooling rate of nearly 10^7 C/s, requiring techniques such as splat-cooling or melt spinning to achieve these cooling rates.

It is also important to note that the geometry and overall volume of the glass body to be cooled with have a significant impact on the cooling rates achieved. While surface cooling rates will more closely follow external temperature changes, the actual cooling rate in the interior of the thicker specimens will necessarily depend upon thermal diffusivity. Thus, it is likely that the cooling rate will vary within the specimen to be cooled and there may be portions of the glass that remain susceptible to crystallization as a result.

Supplementary Reading:

A.K. Varshneya, Fundamentals of Inorganic Glasses (Academic Press, San Diego, CA, 1994), ISBN 0-12-714970-8. And references therein.