1 Introduction

Glasses have been, beyond any doubt, vital materials for the development and well-being of human civilization and are now ubiquitous in our everyday lives. Natural glasses, such as obsidian, are nearly as old as the universe, whereas novel useful glasses are being discovered daily (Zanotto and Mauro, 2017; David Pye, 2016). As summarized in Welcome to the Glass Age, by Morse and Evenson (2016), Glass: the eye of science by Bolt (2017), and Glass and Glass-Ceramic Technologies to Transform the World by Hench (2011), many outstanding innovations can be cited, where glass was the critical material, for instance, optical glass fiber networks that span the globe (Ballato et al., 2017), thin and strong glass sheets for television sets and cell phones (Varshneya and Bihuniak, 2017), high-strength and exceptionally elastic metallic glasses (Li et al., 2019; Shi, 2019), semiconductive chalcogenide glasses (Lin et al., 2018), bioactive glasses for healthcare (Montazerian et al.; Montazerian and Zanotto, 2017), and many other incredible applications described in other chapters.

A diverse variety of glass-forming chemistries exist, having a wide range of structural building blocks from which a glassy material is constructed. The detailed nature of these chemical building blocks and how they are connected depend on the particular nature of the chemical bonding in these systems. In this article, we defend the concept that glass itself is a fascinating state of matter combining aspects of the liquid and solid states. Before elucidating the idea of the glassy state, some basic concepts are defined which will render the modern definition of the glassy state more tangible.

2 Basic Definitions

2.1 Solid

A solid is one of the three traditional, basic states of matter (the others are liquid and gas) where the atomic structure and chemical forces are strong enough to keep that atomic structure and external shape cohesive even when it is not confined in a receptacle.
Solids exhibit certain characteristics that distinguish them from liquids and gases. All solids have, for example, the ability to resist some level of forces applied either perpendicular or parallel to their surface, i.e., normal or shear loads, respectively. Such properties depend on the nature of the atoms that form the solid, the way these atoms are arranged and the bonding characteristic between them (see “Relevant Websites section”).

2.2 Liquid

Liquid is another principal condensed state of matter; intermediate between a gas and crystalline solid. A liquid will retain its volume, but not its shape when it is poured from one vessel to another. The shape variation might occur in a short or very long time; liquids flow under the force of gravity (or even smaller forces) until their shape conforms to that of the container that they occupy (see “Relevant Websites section”).

2.3 Viscous Flow Versus Creep

A characteristic feature of liquids, viscous flow is a cooperative movement of several atomic groups under a positive force field, e.g., gravity. This is quite different from diffusive deformation of solids under stress, such as creeping. While both types of deformation are characterized by rates proportional to the applied stress, they are very distinct on the molecular scale (Hopper and Uhlmann, 1974). The mechanism of creep depends on temperature and applied stress. Dislocation glide or diffusional-flow mechanisms typically dominate creep deformation, and their kinetics is completely distinct from the viscous flow. The most celebrated creep mechanisms are bulk diffusion (Nabarro–Herring creep), grain boundary diffusion (Coble creep), thermally activated and climb-assisted dislocation glide – where the climb is an enabling mechanism, allowing dislocations to move around obstacles. Most of these mechanisms are controlled by vacancy (in single crystals) or grain boundary diffusion (in polycrystals) and are generally triggered after a minimum threshold stress is surpassed, which is composition and temperature dependent. For a detailed description, the reader is invited to study (see “Relevant Websites section”; Poirier, 1985).

2.4 Supercooled Liquid (SCL)

SCL is the liquid state that exists between the melting point or liquidus temperature and the glass transition temperature. Supercooled liquids are thermodynamically metastable and tend to crystallize (Zanotto and Mauro, 2017).

2.5 Crystal

A crystal is a solid material having a well-ordered atomic structure on a periodic lattice. Crystals can be thermodynamically stable or metastable (they can transform into other crystalline structures under pressure or temperature). Crystalline materials may be composed of a single crystal, or they may be polycrystalline (Zanotto and Mauro, 2017). They can be permanently deformed under an external threshold stress.

2.6 Non-Equilibrium Thermodynamic State

The thermodynamic state of a material can be either an equilibrium state or a non-equilibrium state. The values of thermodynamic properties define a thermodynamic equilibrium state. A non-equilibrium state is much more difficult to explain and generally requires the existence of a condition called local thermodynamic equilibrium, which exists when thermodynamic equilibrium occurs locally within a series of small volumes that make up the system. Conversely, a thermodynamic property is any characteristic of a system whose numerical value depends only on the (local) thermodynamic equilibrium state of the system and is independent of how that state was attained (Robert, 2011).

2.7 Ergodic State

Ergodicity denotes a system where the time and ensemble averages of properties are equivalent. This implies that the ergodic system explores a sufficient fraction of its configurational phase space to reach this equivalence (Mauro et al., 2010, 2007).

2.8 Relaxation

Non-equilibrium materials tend to relax toward the equilibrium condition, even in the absence of any external stress field. Their properties are liable to reach the values of the equilibrium state. This change from a non-equilibrium to an equilibrium state is thus called relaxation (Robert, 2011).
2.9 Non-Crystalline Material

A material which lacks the long-range atomic and molecular periodic order of a crystal is called non-crystalline. As first pointed out in the pioneering work of Zachariasen (Zachariasen, 1932) in 1932, the non-crystalline network of oxide glasses is not periodic and symmetrical as in crystals. However, it is not entirely random because the internuclear distances do not fall below a given minimum value.

2.10 Amorphous

An amorphous material (AM) has a non-crystalline structure that differs from that of its isochemical liquid, and does not undergo structural relaxation and the glass transition when heated. Please note the distinction between glasses and amorphous solids; the reader is referred to Gupta (1996) for further details. Both glasses and amorphous solids are examples of non-crystalline materials, but glasses exhibit a glass transition, whereas amorphous solids do not. We will show later that glasses relax to the SCL state then crystallize, whereas amorphous materials crystallize without undergoing any relaxation process. Moreover, AM cannot be made from quenching a liquid; amorphous materials are made, e.g., by evaporation-condensation onto a cold substrate or by the destruction of crystalline structures by high energy.

2.11 Crystallization

Glasses are unstable against the SCL state. All non-crystalline substances (glasses, SCL or AM) are metastable against their crystalline (solid) counterparts. Hence, they tend to reach thermodynamic equilibrium via crystal nucleation and growth. Crystallization is thus the ultimate fate of all non-crystalline materials (Zanotto and Mauro, 2017).

3 The Glassy State

A recent definition of glass reads (Zanotto and Mauro, 2017): "Glass is a non-equilibrium, non-crystalline state of matter that appears solid on a short time scale but continuously relaxes towards the liquid state." This is an intuitive description for the general public. A more detailed definition is "Glass is a non-equilibrium, non-crystalline condensed state of matter that exhibits a glass transition. The structure of glasses is similar to that of their parent supercooled liquids (SCL), and they spontaneously relax toward the SCL state. Their ultimate fate, in the limit of infinite time, is to crystallize." This definition can also be applied to "non-standard" types of glasses, such as liquid crystals, which are partially crystalline but have a vitreous matrix that exhibits a glass transition (Zanotto and Mauro, 2017).

In this chapter, we dwell on the key concepts of the above definition to dig deeper into the glassy state of matter. To understand its key features, we review here the most well-known diagram in glass science (Fig. 1). This figure shows how a first-order thermodynamic property such as molar volume, entropy, or enthalpy varies with temperature for a glass-forming liquid. Through this plot, glass formation is discussed, and the relevant concepts are explained. The different regions in this figure are described as follows (Zanotto and Mauro, 2017):

![Fig. 1 Schematics of how a first-order thermodynamic property, such as volume or enthalpy, varies with temperature for a glass-forming liquid. Four distinct states are shown: liquid, supercooled liquid, glass, and crystal. \( T_m \) = melting point or liquidus temperature, \( T_g \) = glass transition temperature. Glass 1: changed from the SCL at a lower cooling rate, and hence, at a lower glass transition temperature (\( T_{g1} \)) than glass 2; which became frozen at a higher glass transition temperature (\( T_{g2} \)). Most glasses first relax to a SCL state (gray arrow), and then the SCL eventually crystallizes at any temperature below \( T_m \) (green arrows). Adapted from: https://www.youtube.com/watch?v=eYWiFeKt50&start=16s. The glass transition unveiled – A theatrical version.](https://www.youtube.com/watch?v=eYWiFeKt50&start=16s)
(1) In equilibrium, the thermodynamically stable liquids only exist above the melting point \( (T_m) \) or liquidus temperature \( (T_L) \). For any given composition, the liquidus temperature is the highest temperature of thermodynamic equilibrium between the solid and liquid phases, above which any crystal is unstable and will dissolve in the liquid phase. \( T_L \) equals \( T_m \) for congruently melting compounds. Therefore, when the temperature is above the \( T_m \) of a pure system or \( T_L \) for a multi-component system, the liquid is in thermodynamic equilibrium and never crystallizes. Supercooled liquids exist between \( T_m \) and the glass transition temperature, \( T_g \). They are metastable, i.e., a thermodynamic barrier must be overcome for crystal nucleation to take place, but they eventually crystallize (green arrows) after a certain time. If an equilibrium liquid is cooled quickly enough to avoid crystallization, a SCL is obtained. The structure of the liquid rearranges quickly to attain this metastable equilibrium state as the temperature decreases. However, upon continued cooling, as the temperature decreases, the relaxation time of the SCL increases and the system is eventually (temporarily) frozen when the relaxation time exceeds the laboratory observation time. When this happens, the atoms do not have sufficient time to rearrange to the metastable equilibrium state, i.e., the structural reorganization is kinetically arrested. As a result, the enthalpy deviates from the SCL line and follows that of the configurationally frozen system. This freezing of the system occurs continuously and results in a non-equilibrium material known as “glass.” Since the glass transition is a kinetic freezing process, the final enthalpy of glass depends on the cooling rate, which is related to observation time. When the cooling rate is high, the system has less time to relax into a lower energy structure, which leads to greater enthalpy in the final glass. This phenomenon is expressed in Fig. 1. This figure shows that glass 2 (e.g., fiberglass) has higher enthalpy or volume than glass 1 (e.g., a monolithic piece of glass having the same composition as the fiber), since the former is cooled faster than the latter. The temperature range between the equilibrium SCL and the frozen liquid (glass) is defined as the “glass transition” range. The temperature at the intercept between the two lines extrapolated from glassy and liquid enthalpies is the characteristic value of the \( T_g \). Due to its higher cooling rate, glass 2 has a higher \( T_g \) \( (T_{g2}) \), whereas glass 1 has a lower \( T_g \) \( (T_{g1}) \).

### 3.1 Is Glass a Solid or Liquid?

For many decades, researchers have attempted to define glass as either a liquid or, more typically, a solid. However, this binary thinking does not do justice to the true complexity of the glassy state, which combines features of both liquids and solids, and also brings along its unique characteristics. Glass appears to be solid on a typical observation time scale: it has mechanical rigidity and elasticity, it can be scratched and fractured, ring and resonate, just as a solid. However, the structures of all glasses are very similar to those of their corresponding SCL, i.e., a liquid property. It should also be noted that glasses also have a property that is unique to the glassy state due to their non-equilibrium and frozen nature; they undergo spontaneous relaxation towards the SCL state. Additionally, unlike regular solids and liquids, the properties of a glass depend not only on its composition and the current temperature and pressure but also on its entire thermal and pressure histories (Zanotto and Mauro, 2017). Moreover, it has been shown that the glassy state itself cannot be expressed as any linear combination of supercooled liquid states (Mauro et al., 2009b; Mauro and Loucks, 2009). The glassy state is, therefore, unique and can be classified as its own (non-equilibrium) state of matter.

The existence of any glass is transient and temporary since it will continuously relax toward the supercooled liquid state and ultimately crystallize (solidify). Given this combination of solid-like and liquid-like properties, glass could be considered as a special hybrid state of matter (the glassy state), where the solid-like properties are evident when probing its mechanical response on a short timescale, but their non-crystalline structures, spontaneous relaxation to the SCL followed by viscous flow, and crystallization behaviors make them more akin to non-equilibrium “frozen” liquids (Zanotto and Mauro, 2017).

Besides the above discussion on the solid, liquid, and the non-equilibrium nature of glass, there are some key features in the definition of glass that should be elaborated upon. These characteristics include relaxation, glass transition, glass structure, and crystallization.

### 3.2 Relaxation

From relatively low to intermediate viscosities \( (10^0 < \eta < 10^{11} \text{ Pa s}) \), most glass-forming melts usually behave as Newtonian liquids, and immediately relax to relieve any applied stress. However, at extremely high viscosities \( (\eta > 10^{13} \text{ Pa s}) \), when the structural relaxation times become longer than the experimental times, these liquids respond to the “rapid” application of a stress as if they were actually elastic materials. It follows that there must be an intermediate range of viscosities where the response of these melts to the application of a stress is intermediate between the behavior of a liquid and that of an elastic solid. Since this behavior has aspects of both viscous and elastic responses, it is known as viscoelasticity or viscoelastic behavior (Shelby, 2005).

The most common basic model for viscoelasticity, known as the Maxwell model, reads (Shelby, 2005):

\[
\sigma_i = \sigma_0 \exp \left( \frac{G(T)}{\eta(T)} \right) \tag{1}
\]

where \( \sigma_i \) is the stress at time, \( t \), \( \sigma_0 \) is the stress at time zero, \( G(T) \) is the shear modulus, and \( \eta(T) \) is the viscosity. The ratio \( \eta(T)/G(T) \) has the dimensions of time and is equal to the time required for the stress to decay to \( 1/e \), or 0.367, of its initial value. This time, which is commonly represented by \( \tau_g \), is known as the average relaxation time. The stress relaxation time, \( \tau_g \), is thus expressed in terms of viscosity and \( G_\infty \).
where $G_1$ is the shear modulus measured at infinitely high frequency, which changes little with temperature, whereas both $t_R(T)$ and $Z(T)$ vary dramatically with temperature. The viscosity and stress relaxation time are roughly proportional since the temperature dependence of $G_1$ is small. Building on the above definition and considering a typical shear modulus for oxide glasses (in Maxwell’s equation), Angell proposed an operational definition of $T_g$ as the temperature at which the viscosity of the supercooled liquid is equal to $10^{12}$ Pa s (Angell, 1991).

Replacing $Z(T)/G(T)$ by $t_R$, the expression can be written as:

$$t_R(T) = \frac{\eta(T)}{G_\infty}$$

where $G_\infty$ is the shear modulus measured at infinitely high frequency, which changes little with temperature, whereas both $t_R(T)$ and $\eta(T)$ vary dramatically with temperature. The viscosity and stress relaxation time are roughly proportional since the temperature dependence of $G_1$ is small. Building on the above definition and considering a typical shear modulus for oxide glasses (in Maxwell’s equation), Angell proposed an operational definition of $T_g$ as the temperature at which the viscosity of the supercooled liquid is equal to $10^{12}$ Pa s (Angell, 1991).

Replacing $\eta(T)/G(T)$ by $t_R$, the expression can be written as:

$$\sigma_i = \sigma_0 \exp \left( -\frac{t}{t_R(T)} \right)$$

which describes an exponential relaxation curve. If $t_R$ is very small, relaxation will occur so rapidly that normal measurements may indicate that the process is instantaneous. If $t_R$ is very long (e.g., at room temperature for a window glass), the relaxation rate may be so slow that no relaxation is detected in routine measurements. It is reasonably assumed that the infinite frequency shear modulus is essentially temperature independent, the temperature dependence of $t_R$ can be attributed to the temperature dependence of the viscosity. Assuming a typical room temperature value of $G_\infty$ of $\sim 3 \times 10^{10}$ N m$^{-2}$ for oxide glasses, the value of $t_R$ at a viscosity of $10^{12}$ Pa s is 33 s, meaning that significant relaxation occurs after $\sim 33$ s. It follows that relaxation at temperatures in the glass transition range would be expected to occur over times ranging from hours to seconds, as the viscosity decreases with increasing temperature. Since most experimental measurements of $T_g$ involve heating specimens at rates of $3-20$ K min$^{-1}$, we expect that these measurements will indicate relaxation processes occurring on similar timescales ($\sim 1/10$ min = 6 s) and that the $T_g$ values refer to viscosities of the order of $10^{11}$ to $10^{12}$ Pa s. This relaxation concept is instrumental in understanding the glass transition phenomenon.

The structural relaxation process can be best appreciated in isothermal experiments, for instance by following refractive index changes of a glass with time at several temperatures below the original $T_g$, as shown schematically in Fig. 2. Such a process has been frequently formulated by the most traditional relaxation equation, often called the KWW (Kohlrausch–William–Watts) function, as follow (Hodge, 1994):

$$\phi(t, T) = \frac{p(t) - p_\infty(T)}{p_0(T) - p_\infty(T)} = \exp \left[ -\left( \frac{t}{\tau_k(T)} \right)^\beta(T) \right]$$

where $\phi$ is the relaxation parameter, $p$ is a property that varies during relaxation (for instance, density, specific heat, or refractive index), $p_\infty$ is the property value for a treatment time long enough for full relaxation, $p_0$ is the initial value of that property, $\beta$ is a dimensionless factor, $0 < \beta \leq 1$, and $\tau_k$ is the characteristic relaxation time, which can be calculated by the following equation:

$$\tau_k(T) = \frac{\beta(T) \tau_R(T)}{\Gamma(1/\beta)}$$

where $\Gamma$ is the gamma function, and $\tau_R$ is the average relaxation time, which can be calculated by the Maxwell equation, Eq. (2), using the values of $\eta$ and $G_\infty$ ($10-50$ GPa for silicate glasses).

![Fig. 2](image-url) Time dependence of the refractive index for lead metasilicate glass. Relaxation experiments were performed at 25K below the original glass transition temperature, where the sample was previously treated to equilibrate ($T_g - 25 = 651$K). The full line is the regression with the KWW equation. The horizontal dotted line shows the refractive index at the initial time. Reproduced from Lancelotti, R.F., Cassar, D.R., Peitl, O., Zanotto, E.D., 2019. Refractive Index Investigation of Structural Relaxation of Oxide Glasses, (in preparation).
From relaxation experiments, such as that shown in Fig. 2, one can fit Eq. (4) to calculate the values of $\beta$ and $\tau_R$ for a given glass at different temperatures. The KWW equation usually fits quite well the experimental relaxation kinetics carried out not far below the original $T_g$ (say, down to $T_g - 30K$). However, it does not have any predictive power for the variation of relaxation time with temperature, $\tau(T)$, because $\beta$ also varies with temperature. The value of $\beta$ itself is relevant because it gives a measure of the width of the distribution of relaxation times of the numerous “cooperatively rearranging regions” (CRR) that exist in glass formers (Hodge, 1994). The lower the value of $\beta$, the wider the relaxation time distribution.

More elaborate empirical models exist, such as the TNM model (Tool–Narayanaswamy–Moynihan) (Hodge, 1994), and the modified recent MAP model (Mauro–Allan–Potuzak) (Mauro et al., 2009a; Guo et al., 2018; Mauro and Mauro, 2018; Wilkinson et al., 2018). The MAP can be used to describe glass relaxation. More details about the implementation of the KWW and MAP equations are provided in Guo et al. (2018) and Mauro and Mauro (2018). Moreover, recently a Python-based code was designed by Wilkinson et al. to retrieve the evolution of the fictive temperature, viscosity, and relaxation time using the inputs from the temperature path and set of material properties, including the viscosity parameters (Wilkinson et al., 2018).

Fig. 2 shows the structural relaxation kinetics at 25K below the fictive temperature temperatures for lead metasilicate glass (Lancelotti et al., 2019). The refractive index measurements proved to be a very good technique to follow the relaxation during isothermal treatments because the uncertainty of the measurements was only in the fifth decimal place. The KWW equation fitted the experimental data quite well; the full line is a regression obtained using the model. The dotted line represents the initial value of the refractive index for all temperatures. The fitted parameter of the KWW equation, as well as the average relaxation time, calculated by Eq. (2), are shown in Table 1 (Lancelotti et al., 2019).

### 3.3 Glass Transition

Glasses only exist below their respective glass transition temperature, $T_g$. They are thermodynamically unstable and spontaneously relax toward the supercooled liquid state at any nonzero temperature (gray arrow in Fig. 1). The glass transition takes place at $T_g$, the temperature where the experimental or observation time, $t_{obs}$, is similar to the average structural relaxation time of the SCL, $\tau_R$. On the heating path, a glass changes to a SCL at $T_g$, whereas on the cooling path the SCL temporarily freezes into the glassy state. In isothermal experiments, at any positive temperature, above or below $T_g$, for sufficiently long times ($t_{obs} \gg \tau_R$), any SCL or glass relaxes, and then eventually crystallizes to a solid with well-organized atomic structures at short, medium and long range, which is thermodynamically stable below $T_m$ (arrows in Fig. 1; Zanotto and Mauro, 2017). $T_g$ depends on the cooling rate (observation time). There is a standard value called the standard calorimetric glass transition temperature ($T_g^s$), which is measured using a differential scanning calorimetry (DSC) at a heating rate of 10 K min$^{-1}$. For oxide glasses, this $T_g^s$ typically corresponds to a viscosity of ca. 10$^{12}$ Pa s. Furthermore, $T_g$ varies with composition, thermal history, and mechanical history. Whereas the crystallization of liquid results in an abrupt discontinuity in thermodynamic variables (e.g., volume and enthalpy), the glass transition is not a thermodynamic phase transition. A thermodynamic consequence of this kinetic transition is that configurational degrees of freedom in the glass are (temporarily) frozen, leading to a sharp loss of second-order thermodynamic properties, such as heat capacity and thermal expansion coefficient (Guo et al., 2018).

This event and key parameters of the calorimetric glass transition are illustrated in Fig. 3. The changes of the isobaric heat capacity ($C_p$) with temperature are recorded for a calcium metaphosphate glass during the DSC upscan (heating) and its corresponding liquid during the subsequent downscan (cooling) at the standard rate of 10 K min$^{-1}$ (Zheng et al., 2019; Yue, 2008). The glass transition occurs over a range of temperatures ($\Delta T_g^s$, in Fig. 3), but it is convenient to define a single temperature as an indication of the onset of the glass transition range for a glass. This temperature is termed the standard glass transition temperature ($T_g$) (Zheng et al., 2019). The standard $T_g$ value is determined as the crossing point temperature of the extrapolated $C_{p_{ex}}$ line and the extrapolated line of the rapidly rising $C_p$ line. This $T_g$ value is equal to the temperature ($T_g^{onset}$) corresponding to the inflection point of the $C_p$ drop line during cooling (see the blue filled circle in Fig. 3). As such, the glass-to-liquid transition during heating is manifested by $\Delta C_p(T_g)$, i.e., the $C_p$ jump from glass $C_p$ at $T_g$ (denoted $C_{p_{ex}}$) to liquid $C_p$ at the ending temperature of glass-to-liquid transition ($T_g^{onset}$) (denoted $C_p$) (Yue, 2008; Guo et al., 2011). The $T_g$ of different glass systems can vary from below 50K to above 1500K (Zheng et al., 2019).

### 3.3.1 Ergodicity

The glass transition is intimately connected to the notion of ergodicity. For an ergodic system, the time and ensemble averages of properties are equivalent and implies that the system explores a sufficient fraction of its configurational phase space to reach this

### Table 1

<table>
<thead>
<tr>
<th>$T(K)$</th>
<th>$\tau_A(s)$</th>
<th>$\beta(T)$</th>
<th>$\tau_R(s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>651</td>
<td>72,617</td>
<td>0.59</td>
<td>111,718</td>
</tr>
</tbody>
</table>

Fig. 3  Temperature dependences of the isobaric heat capacity ($C_p$) for calcium metaphosphate glass (CaP$_2$O$_5$), which were determined using DSC during the heating-cooling cycle (rate: 10 K min$^{-1}$). The glass–liquid transition during upscan is featured by the $C_p$ jump, $\Delta C_p(T_g)$, whereas the liquid–glass transition is reflected by the $C_p$ drop. The onset temperature of the glass–liquid transition, i.e., the intercept between the extrapolated glass $C_p$ line and the line with the maximum tangent of the $C_p$ rising curve, is defined as the standard glass transition temperature $T_p$. Reproduced with permission from Yue, Y., 2008. Characteristic temperatures of enthalpy relaxation in glass. Journal of Non-Crystalline Solids 354 (12–13), 1112–1118.

The Glassy State

equivalence (Mauro et al., 2010, 2007). However, a system that is initially ergodic can become non-ergodic, i.e., if sufficient configurational degrees of freedom are lost. This breakdown of ergodicity can occur either discontinuously or continuously, depending upon the details of the system. Whether or not a system is ergodic is a question of timescale. There are two relevant time scales involved when an experiment is taking place. One is the internal time scale ($t_{int}$) on which the dynamics of the system occur, which is essentially a relaxation time over which a system loses “memory” of its preceding states. This internal time scale is related to $\tau_R$. The other is the external time scale ($t_{ext}$) on which properties are measured, which defines a measurement window over which the system is observed. The Deborah number (Reiner, 1964) of an experiment is defined as the ratio of internal to external time scales,

$$D = \frac{t_{int}}{t_{ext}}$$

A large Deborah number ($D \gg 1$, $\tau_{int} \gg \tau_{ext}$) indicates that the system visits only a small subset of the available points in phase space during the external (i.e., observation) time scale. Hence, a system with a large Deborah number is non-ergodic. On the contrary, a very small Deborah number ($D \ll 1$, $\tau_{int} \ll \tau_{ext}$) means that the system can explore a greater portion of phase space during the observation time, which leads to an ergodic system. Therefore, both the internal relaxation time of a system and the external observation time determine the ergodicity of the system.

Palmer (1982) introduced the notion of “broken ergodicity,” in which glass can be described as an ensemble of components of the phase space, where each component exhibits internal ergodicity, but transitions between components are not allowed. This breakdown of ergodicity occurs when the Deborah number of the system is near unity, $D \approx 1$. This breakdown is the most fundamental definition of the glass transition, i.e., where the internal relaxation time of a glass-forming system is equal to an external observation time scale ($t_{obs} = t_{int}$). The transition between ergodic and nonergodic states, where $D \approx 1$, corresponds to the glass transition. For any realistic system, the loss of ergodicity is a gradual process, i.e., the glass transition involves a continuous breakdown of ergodicity. Thus, the glass transition is fundamentally a process in which a supercooled, ergodic liquid is gradually frozen into a non-equilibrium, non-ergodic glassy state. The glassy state can be observed only when the relaxation time scale of the system becomes much longer than the observation time scale, i.e., the glass transition only takes place when a finite observation time is defined (Varshneya and Mauro, 2019).

In summary, given the above definition, $T_g$ refers to a temperature where the time of observation (of an experiment), $t_{obs}$, is of the same order as the average structural relaxation time, $\tau_R$, of the supercooled liquid; $t_{obs} \sim \tau_R$. According to Maxwell’s relation, $\tau_R = \eta/G_\infty$. For typical oxide glasses in classical laboratory experiments by, e.g., DSC or dilatometer, carried out at 5–20 K min$^{-1}$, $\eta(\tau_R) \sim 10^{12}$ Pa s and $G_\infty \sim 3 \times 10^{10}$ Pa, hence, $\tau_R \sim 33$ s (Donth, 2001). Additionally, at $T_g$ the $\tau_R/t_{obs}$ ratio, the Deborah number, is near unity.

As well as these theoretical concepts, various experimental approaches have been developed to characterize and explain glass transition. As already pointed out, one of the most effective experimental approaches is via DSC studies, which is probably the most sensitive technique to the (small) energy fluctuation during glass transition and relaxation. The glass transition traced by DSC is termed the calorimetric glass transition. $T_g$ can also be measured by thermal expansion or density measurements. The value of $T_g$ for the same glass composition could be slightly different using various measurement methods, even at the same heating rate. It is known that $T_g$ has dynamic characteristic values since it shifts to higher temperatures with an increasing heating rate or cooling rate (Shelby, 2005; Varshneya and Mauro, 2019). To compare the dynamics and physical properties of different glass systems, a standard, unified approach for measuring $T_g$ should be defined. For example, Yue compared the calorimetric glass transition temperature ($T_g\textsubscript{DSC}$) directly measured by DSC at 10 K min$^{-1}$ with the $T_g\textsubscript{vis}$ indirectly determined at the viscosity of $\eta = 10^{12}$ Pa s.
(Yue, 2008, 2009), with $T_{g,DSC}$ being defined as the onset temperature of the calorimetric glass transition peak (Fig. 3). As mentioned above, the $C_p$ curve is normally obtained at the standard upscan rate of 10 K min$^{-1}$ (equal to the first downscan rate). He showed that the two sets of $T_g$ values remarkably coincide for oxide glasses (Yue, 2008, 2009). The agreement between $T_{g,vis}$ and $T_{g,DSC}$ can be used for assigning the standard $T_g$. This allows a direct comparison of the glass transition temperatures among different glassy systems.

### 3.4 Glass Structure

Oxide glasses, such as traditional soda-lime silicate glasses, have network structures composed of SiO$_4$ tetrahedral building blocks connected by mixed ionic-covalent bonding. Chalcogenide glasses, which contains one or more chalcogens (sulfur, selenium, and tellurium) and exclude oxygen, and exclude oxygen and sodium and potassium. Metal glasses consist mainly of icosahedral units with metallic bonding. Organic polymeric glasses are made through the cross-linking of molecular chains involving van der Waals bonding between chains and covalent intra-molecular bonding. In the recently discovered metal-organic framework glasses, tetrahedral units are connected via coordination bonds. Water can also be quenched into a glassy state and comprises tetrahedral units connected by hydrogen bonds. It is these different types of bonds, resulting from the various electronic structures of the constituent atoms, that lead to different structures, unique state and novel properties of glassy materials (Zheng et al., 2019; Varshneya and Mauro, 2019).

Experimental data and computer simulations of different supercooled liquids and glasses show that their atomic structures below $T_g$ are quite similar to those of their parent supercooled liquid just above $T_g$ (Zanotto and Mauro, 2017; Bykov et al., 2009). Obviously, glasses do not exhibit the ordered crystalline structure as most other ceramic materials but, instead, have a disordered long-range structure with some order at short- and medium-range (3rd-4th neighbors). The most widely used glasses, by far, are oxide glasses, mainly formed from SiO$_2$, B$_2$O$_3$, P$_2$O$_5$, As$_2$O$_3$, Sb$_2$O$_3$, GeO$_2$, TeO$_2$, Al$_2$O$_3$, alkali or alkaline earth oxides, etc. The literature on glass structure is vast because of persistent interest in solid-state chemistry, condensed matter physics, geosciences, and medicine.

Here we aim to highlight a few basic concepts; exemplifying with pure SiO$_2$ and some of its derivatives. Silicate-based glasses are quite crucial in technology, e.g., optical fibers, electronic screens, architectural materials, and bioactive glasses, but also exist in nature, e.g., obsidian and Libyan Desert glass. Crystalline forms of silica are comprised of a three-dimensionally linked, corner-shared network of SiO$_4$ tetrahedra (cf. Fig. 4(a)). The oxygen links between the Si$^{4+}$ cations (…Si–O–Si–…) is called network forming or "bridging" oxygen (BO). When an oxide of another element, typically an alkali or alkaline earth oxide, with +1 or +2 valence, is added to liquid silica, there are too many oxygen anions (O$^{2-}$) which cannot all bond to two tetrahedrally coordinated Si$^{4+}$ cations. As a result, some must be connected to only one oxygen of the SiO$_4$ group. This oxygen is then called "non-bridging" oxygen (NBO). A two-dimensional view of a SiO$_2$–CaO–Na$_2$O glass showing BO and NBO is shown in Fig. 4(b) (Stebbins, 2016). In standard models, exactly two NBO are formed from one BO and one extra O$^{2-}$ ion (see Eq. (7) and Fig. 5(a)).

$$\text{Si} - \text{O} - \text{Si} + \text{M}_2\text{O} \leftrightarrow 2\text{Si} - \text{O}^- + 2\text{M}^+ \quad (7)$$

Contrary to Si in binary silicate glasses, B in borate glasses has two coordination numbers with oxygen, $^{III}	ext{B}$, and $^{IV}	ext{B}$. In GeO$_2$ based glasses, $^{IV}	ext{Ge}$, $^{V}	ext{Ge}$, and $^{VI}	ext{Ge}$ are observed in glass structures. In pure B$_2$O$_3$ and GeO$_2$ glasses, only the lowest coordination states $^{III}	ext{B}$ and $^{IV}	ext{Ge}$ exist. As an alkali oxide is added, NBOs are not necessarily formed as in silicates, but to accommodate the

![Fig. 4](image-url)  
**Fig. 4** Sketch of (a) SiO$_4$ tetrahedra and (b) two-dimensional view of soda-lime silicate glass structure comprised of a corner-shared network of SiO$_4$ tetrahedra, bridging (BO) and non-bridging oxygens (NBO), connected with Na$^+$ and Ca$^{2+}$ cations. Adapted from Maraghechi, H., Rajabipour, F., Pantano, C.G., Burgos, W.D., 2016. Effect of calcium on dissolution and precipitation reactions of amorphous silica at high alkalinity. Cement and Concrete Research 87, 1–13, with permission from Elsevier.
added oxide ion, the coordination of the network cation, e.g., IVB and V,IGe increases (cf. Fig. 5(b)). As a result, the modifier cations are coordinated by bridging O atoms, which have partial negative charges, e.g., $\text{[IIIB-O-IVB]}^{1/4}$ or $\text{[IVGe-O-VGe]}^{1/5}$. When higher amounts of alkali oxide are added, NBOs form and the coordination of network formers decreases again, finally being dominated by the low-coordination numbers (Stebbins, 2016).

The effects of different cations are usually explained by the "cation field strength," which is the valence divided by the sum of the cation and oxide ion radii (e.g., $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$) (Brown et al., 2019). Multiple modifier cations (M) present in the melt compete for the formation of small coordination shells with short M-NBO distances. The higher field strength cation is expected to win. This phenomenon is also observed in crystals. For example, $\text{Ca}^{2+}$ in crystalline diopside has 4 NBO and 4 BO neighbors, while $\text{Mg}^{2+}$ has 6 neighbors, all NBO. Modifier cations in the glass will thus interact with both NBO and BO. The interactions in liquids are dynamic, transient, and liable to be important in breaking BO/C0Si bonds, activating viscous flow.

Mixing of different modifier cations will change the configurational entropy, affecting viscosity curve and thermodynamic variables. For example, contrasting to the crystal, randomized distribution of modifiers in glass and liquid contribute largely to the entropy of melting (Brown et al., 2019; Allwardt and Stebbins, 2004). The 3D scheme for the structure of an yttrium aluminosilicate glass ($\text{Y}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$) in Fig. 6 proves how a broad range of possibilities for obtaining a disordered structure disordering is envisaged. This glass is used in in situ radiotherapies, irradiating tumors by the radioactive yttrium isotope ($^{90}\text{Y}$). The $^{90}\text{Y}$ cation can have variable coordination numbers in melts and glasses, which varies in complex ways with composition, temperature, and pressure (Christie and Tilocca, 2012). Therefore, elucidation of structure-property relationship is of the utmost importance in many applications.

### 3.5 Crystallization

Glasses are formed when the kinetic demands of thermodynamic equilibrium are not met by manipulating the chemical composition, sample size, or cooling rate of a melt. Following the most common route of glass formation, i.e., quenching from a melt, any SCL can, in principle, be vitrified with a sufficiently high cooling rate (critical cooling rate) that is enough to avert crystallization. It should be stressed once more that when cooling a liquid, vitrification occurs at a temperature $T_g$ where the structural relaxation time of the SCL becomes equal to or longer than the experimental observation time. Understanding the role of critical factors that determine the vitrification and crystallization processes, such as glass composition, the structure of the SCL, thermal history, and diffusion processes, is a vital step for the study and development of new materials that readily form glasses, or for the successful progress of glass-ceramic science and technology (Montazerian et al., 2015; Davis and Zanotto, 2017).

#### 3.5.1 Crystal nucleation

Nucleation and crystal growth are the two essential stages of crystallization; nucleation is the homogeneous or induced (catalyzed) formation of nanosized critical crystal clusters (nuclei), which is followed by their spontaneous growth becoming crystals. For glass forming compositions, homogeneous nucleation is typically observed in a temperature range (not far from $T_g$) well below the
temperature of maximum crystal growth rates, whereas heterogeneous nucleation rate versus temperature curves are often close and even overlap with those of crystal growth (Fokin et al., 2006).

Crystallization of glasses (or more correctly, of supercooled liquids) is an exothermic process that can be readily detected by thermal analysis techniques, such as DSC and DTA. In a typical DSC curve of a glass, crystallization is displayed as an exothermic peak after the glass transition, $T_g$, as depicted in Fig. 7. For stoichiometric compositions, the crystallization temperature ($T_c$), corresponds to the peak temperature in a DSC trace, whereas the onset crystallization temperature is called $T_x$. Upon continuous heating, in the end, an endothermic peak is a signature of melting ($T_L$). For off-stoichiometric compositions, two or more crystallization and melting peaks may appear (Fig. 7; Guo et al., 2018).

Detailed knowledge of the thermodynamics and kinetics of crystal nucleation and growth is crucial, either to avoid devitrification or to control the crystallization process. Glass crystallization-related phenomena, including crystal nucleation, induction periods for nucleation, crystal growth, glass stability against devitrification, and glass forming ability are critical parameters in both
academic and industrial studies. These phenomena are usually studied by optical and electron microscopy, X-ray diffraction (XRD), nuclear magnetic resonance (NMR), or DSC tests (Guo et al., 2018; Fokin et al., 2006).

In summary, supercooled liquids are metastable against their crystalline (solid) counterparts, the thermodynamically stable state for \( T < T_m \). Hence any SCL will tend to crystallize via crystal nucleation which is then followed by spontaneous growth. Nucleation is a stochastic process, hence, after some average time \( \tau_N \) (which depends on the material’s chemical composition and the temperature), one or more critical crystalline nuclei will form in the SCL. Once the nuclei have reached a critical size, crystal growth spontaneously starts and the material solidifies, transforming into a polycrystalline solid.

In steady-state nucleation conditions, which are typically observed above \( T_g \), the average number of nuclei \( (N_t) \) per volume \( (V) \) equals \( N_t = \frac{I_a}{V} \cdot t \), where \( I_a(m^{-3} s^{-1}) \) is the steady-state nucleation rate at the temperature of study. In this condition, the average nucleation time is \( \tau_N = \frac{I_a}{I_s} \cdot V^{-1} \). However, for very deep supercoolings \( (T \ll T_g) \), where the nucleation induction times, \( \tau_{ind} \), are significant, \( \tau_{ind} \) must be added to \( \frac{I_a}{I_s} \cdot V^{-1} \), hence \( \tau_N \approx \frac{I_a}{I_s} \cdot V^{-1} + \tau_{ind} \) (Fokin et al., 2006; Deubener et al., 2017). \( \tau_N \) and \( \tau_{ind} \) are shown in Fig. 8, which is an example for a \( N_t vs. \) time plot in a fixed temperature (the crystal nucleation and growth temperatures are \( T_N = 430^\circ C \) and \( T_G = 626^\circ C \), respectively). Hence, to estimate \( \tau_N \) at very deep supercoolings, one has to extrapolate experimental values of steady-state nucleation rates and obtain nucleation induction times, which are typically measured at and above \( T_g \) down to very low temperatures. In any case, the nucleation times are always finite; therefore for infinitely long times, all supercooled liquids should crystallize by nucleation and growth (Fig. 8(b)).

### 3.5.2 Crystal growth

As soon as the nucleation conditions are attained and some nuclei reach the critical size, crystal growth spontaneously proceeds (there is no thermodynamic barrier for crystal growth). The transport of atoms at the interface between the nucleus and the surrounding SCL matrix is of great importance with regard to kinetic and morphological processes of crystal growth. Three basic models are available to describe crystal growth rates: normal growth, screw dislocation growth, and secondary nucleation or two-dimensional growth (Nascimento et al., 2004, 2011).

During Normal (or Continuous) Growth, the crystal/liquid interface is pictured as rough at an atomic scale. Growth takes place at step sites, which represent a sizable fraction \((0.5–1.0)\) of the interfacial sites. When this fraction does not change appreciably with temperature, the growth rate, \( U(T) \), can be expressed as (Nascimento et al., 2004, 2011):

\[
U = f D \frac{4d_0}{k_BT} \left[1 - \exp\left(-\frac{\Delta G}{k_BT}\right)\right]
\] (8)

where \( f \) is close to unity, \( \Delta G \) is the Gibbs free energy, \( D \) is the effective diffusion coefficient controlling material transport to the interface, and \( d_0 \) is a jump distance (a few Angstrom).

In the Screw Dislocation growth model, the interface is assumed to be smooth but imperfect at an atomic scale. Crystal growth takes place at a few step sites provided by screw dislocations that intersect the interface. The growth rate is also given by Eq. (8), where \( f \) is the fraction of preferred growth sites (on the dislocation ledges) at the interface. In this case, \( f \ll 1 \) is given approximately by \( f \approx (T_m - T)/(2\pi T_m) \) (Nascimento et al., 2011).

In the case of Secondary Surface Nucleation or Two-dimensional growth, the interface is smooth and perfect at an atomic scale and thus free of intersecting screw dislocations and growth sites. Growth then takes place by the formation and growth of new two-dimensional nuclei at the interface (Nascimento et al., 2004, 2011).
In both crystal nucleation and growth, the interplay between an increasing driving force for crystallization, $\Delta G$, and decreasing diffusion coefficient (e.g., increase in viscosity) with decreasing temperature results in a maximum of the $I(T)$ and $U(T)$ curves. The maximum growth rate is usually located at higher temperatures than that of the maximum of the (homogeneous) steady-state nucleation rate (Fig. 9; Schmelzer et al., 2015).

### 3.5.3 Overall crystallization

The overall crystallization of supercooled liquids occurs by a combination of crystal nucleation and growth. The kinetics of such processes is usually described by a theory independently derived between 1937 and 1941 by Johnson & Mehl, Avrami, and Kolmogorov (JMAK theory) (Fokin et al., 2006). In this approach, the evolution of the volume fraction of the crystalline phase is described as a function of time, accounting simultaneously for nucleation and growth. According to this model, the volume fraction of the new phase (in this case a crystal) is given by Eq. (9) (Shelby, 2005; Varshneya and Mauro, 2019; Šesták and Šimon, 2013).

$$z(t) = 1 - \exp\left(-g \int_0^t I(T) \left[\int_0^t U(T) dt'\right]^n dt\right)$$  \hspace{1cm} (9)

where $g$ is a shape factor that depends on the shape of crystals. If the nucleation ($I$) and growth ($U$) rates are constant throughout the transformation, and the crystals are spherical, Eq. (9) can be rewritten as:

$$z(t) = 1 - \exp\left[-gI^3t^n\right]$$  \hspace{1cm} (10)

When the number of growing crystals, $N_o$, does not change with time (typical for fast heterogeneous nucleation on a finite number of active sites, or from quenched-in, athermal nuclei), Eq. (9) transforms to:

$$z(t) = 1 - \exp[-gN_oU^3t^n]$$  \hspace{1cm} (11)

Avrami proposed that, in the general case, the following relation should be used:

$$z(t) = 1 - \exp[-Kt^n]$$  \hspace{1cm} (12)

where $K$ represents the so-called rate constant, and $n$ is the Avrami coefficient. In typical applications, Eq. (12) is used in the form

$$\ln(-\ln(1 - z)) = \ln K + n \ln t$$  \hspace{1cm} (13)

The values of $K$ and $n$ can be estimated by fitting the experimental data of $z(t)$ (crystal volume fraction of isothermally heat-treated glass) to Eq. (13). Thus, the coefficient $K$ includes $I$ and $U$, or $N_o$ and $U$.

In Eq. (13), $n$ is called the Avrami coefficient, and depends on both nucleation and growth mechanisms, as shown in Table 2. The knowledge of that coefficient is very helpful to understand the mechanism of phase transformation at any given temperature (Illeková and Šesták, 2013).

The JMAK theory has been used in numerous studies to analyze experimental data and determine the degree of crystallinity as a function of time in both isothermal and non-isothermal heat treatments of glass systems. Emphasis is usually given to determining the so-called Avrami coefficient $m = n + 1$ obtained from the slopes of experimental $\ln[\ln(1 - z)^{-1}]$ versus $\ln(t)$ plots. However, there is frequently some uncertainty in such analyses, because different combinations of nucleation and growth laws may lead to the same Avrami coefficient. For this reason, a separate investigation of the growth kinetics may be required to reach definite conclusions. It is important to underline that the JMAK theory, as given by Eqs. (10)-(12), does not apply to non-isothermal processes. These three equations are derived from the assumption of constant nucleation and growth rates, which are not achieved in non-isothermal processes. Therefore, in non-isothermal cases, the general relationships, Eq. (9), must be used to describe overall crystallization (Gutzow and Schmelzer, 1995).
Finally, we should emphasize that the extremely good glass-forming liquids known so far – Na₂O·Al₂O₃·6SiO₂ (albite) and B₂O₃ – will also crystallize if they are subjected to sufficient long thermal treatment. This is because their maximum homogeneous nucleation rates are located well below their glass transition temperatures, in a region of very high viscosity, which leads to extremely long nucleation time-lags and low nucleation rates (Zanotto and Cassan, 2017). However, under adequate conditions, they should crystallize.

4 Summary and Conclusions

It is estimated that more than 10⁷ inorganic glasses have already been made (Zanotto and Coutinho, 2004), and billions of others could still be made, however, crystallization (solidification) must be avoided for vitrification. Hence only a small fraction of the possible compositions can be effortlessly vitrified.

Are glasses solids or liquids? We defend that glasses are neither solids nor liquids; instead, they display ambivalent properties: of solids – they ring, resonate, scratch and fracture – and liquids, they have an identical structure as their parent liquids, and also show the unique property of spontaneously relaxing towards the SCL state, even without the influence of any external stress. Moreover, the glassy state itself cannot be expressed as any linear combination of supercooled liquid states.

All glasses are trapped in a frozen, transient state; they will relax toward the supercooled liquid state and ultimately crystallize. The relaxation and crystallization times strongly depend on their chemical composition and on how far below its $T_g$ the glass is being studied. If a glass is being tested only a few degrees below its $T_g$, these processes will only take place in geological time scales. Therefore, in our opinion, the glassy state is a unique non-ergodic, non-equilibrium, non-crystalline state of matter that continuously relaxes and finally crystallizes. The modern definition of glass revised and discussed here can be applied to all types of glasses.

Acknowledgments

The authors are grateful to the São Paulo Research Foundation (FAPESP, #2013/07793-6) – CEPID/CeRTEV – for the financial support of this work and the post-doctoral fellowship granted to Maziar Montazerian (#2015/13314-9). We are also indebted to Prof. John C. Mauro for his most useful insights when we co-authored Zanotto and Mauro (2017), which “nucleated” this chapter. This article is thus an extended version of Zanotto and Mauro (2017).

References


Relevant Websites
Britannica
Liquid Chemistry, Properties, & Facts.
https://www.britannica.com/science/solid-state-of-matter
Britannica
https://en.wikipedia.org/wiki/Creep_(deformation)
Wikipedia
Creep (deformation).