



The glassy state of matter: Its definition and ultimate fate



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ABSTRACT

The objective of this communication is to clarify the meanings of solid and liquid, to dwell on the ultimate fate of glass in the limit of infinitely long time, and to propose a modern, improved definition of glass. We review the four characteristic states of matter related to vitrification: the stable equilibrium liquid (L), the metastable supercooled liquid (SCL), the unstable nonequilibrium glass (G), and the stable crystal (C). We also discuss some relevant terms and phenomena, including glass transition, crystallization, non-crystalline, amorphous, solid, and frozen. We review several previously published definitions of glass and finally propose an improved definition in two alternative forms. The first improved definition is: “Glass is a nonequilibrium, 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 and young students. An alternative, more detailed definition to be understood and used by advanced students, researchers, and professors is: “Glass is a nonequilibrium, 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 is for experts who understand the meaning of glass transition.

1. Introduction

Natural glasses, such as obsidian and amber, have existed long before the emergence of life on earth. Synthetic oxide glasses were discovered circa 6,000 years ago and are now ubiquitous in domestic and high technology applications [1]. In fact, glass has been so essential for the development of today's modern civilization, a recent argument proposes that we are now living in the Glass Age [2].

The word “glass” has been traditionally associated with inorganic products of fusion that have been cooled to a rigid condition without crystallizing, a definition that is used in several procedures in glass technology, such as the DIN, ISO, and ASTM standards. Numerous traditional oxide glasses, and some relatively novel inorganic glasses, such as chalcogenide, fluoride, bromide, oxyfluoride, oxynitride, and others (approximately 400,000 compositions are registered in the SciGlass database [3]), as well as an increasing number of vitreous organic, polymer, and metallic alloys, have been discovered in the past century. Most recently, glasses have even been made from hybrid metal-organic framework materials [4]. It is possible that most water in the Universe may be glassy [5].

To understand some of the key features and the nature of glasses, it is educative to start with one of the most well-known diagrams in glass

science: the enthalpy versus temperature plot, from above the melting point down to the absolute zero (Fig. 1). The different regions in Fig. 1 can be defined as:

- i. In equilibrium, the thermodynamically stable liquids (L) only exist above the melting point or liquidus temperature, T_m . They never crystallize.
- ii. Supercooled liquids (SCL) 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, and they eventually crystallize (red arrows) after a certain time;
- iii. Glasses (G) exist below the 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, τ_R . On the heating path, a glass changes to a SCL at T_g . 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 (arrows in Fig. 1).
- iv. Crystals (C) are true solids with well-organized atomic structures at

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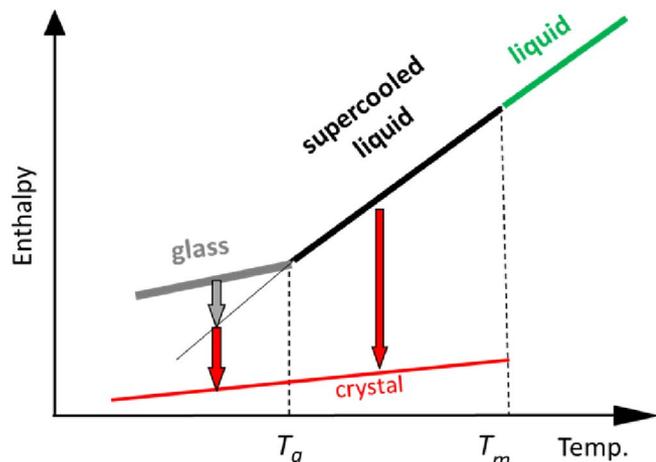


Fig. 1. Schematic enthalpy versus temperature plot for a glass-forming substance showing four distinct states: liquid (L), supercooled liquid (SCL), glass (G), and crystal (C). T_m = melting point or liquidus temperature, T_g = glass transition temperature.

short, medium and long range, which are thermodynamically stable below T_m .

Another vital concept related to supercooled liquids, which is not well-known within the glass research community, is the liquid stability limit or kinetic spinodal temperature, T_{KS} [6–8]. It is defined as the temperature at which the average relaxation time, τ_R , of the supercooled liquid is equal to the average time required to form the first critical crystalline nucleus in the supercooled liquid, τ_N ($\tau_N = (I_{st}V)^{-1}$, where $I_{st}[\text{m}^{-3}\text{s}^{-1}]$ is the steady-state nucleation rate at the temperature of study and $V[\text{m}^3]$ is the sample volume). Immediately after the first nucleation event, the supercooled liquid becomes unstable against crystallization and crystal growth immediately proceeds. After some time (which is material and temperature dependent), it will fully crystallize. Above T_{KS} the average relaxation time of the SCL is shorter than the average crystal nucleation time, whereas for $T < T_{KS}$ the average nucleation time is shorter than the average relaxation time. These two characteristic times are depicted in Fig. 2. In path a, the

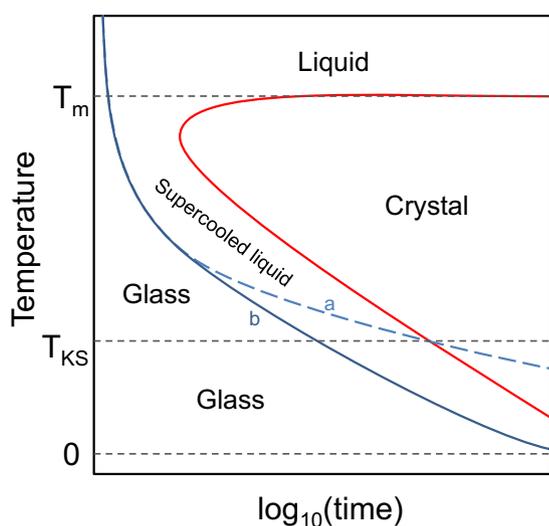


Fig. 2. Schematic representation of the average structural relaxation time of a supercooled liquid, τ_R (blue curves a and b) and the average nucleation time, τ_N (red line) as a function of the temperature. T_{KS} is the kinetic spinodal temperature. In path a, the average relaxation time curves of a supercooled liquid (dashed blue line) crosses the crystal nucleation time curve at T_{KS} , whereas in path b (blue line), they never cross. Both paths are theoretically possible.

average relaxation time curve of a supercooled liquid (dashed blue line) crosses the crystal nucleation time curve (red line) at T_{KS} , whereas in path b (blue line), they never cross. Both paths are theoretically possible, but this is still an open problem in glass science.

2. Current definitions of “glass”

Many definitions of glass have been proposed throughout the past two centuries. Here we review some of the most popular.

2.1. Definitions in glass textbooks

In glass science and technology textbooks one finds several different definitions. In a historical monograph published in 1933, the Russian chemist Gustav Heinrich Johan Apollon Tammann [9] stated that “glasses are undercooled solidified melts.” Forty years later, Robert H. Doremus [10] pointed out that typical definitions of glass are represented by the following: “a material formed by cooling from the normal liquid state which has shown no discontinuous change in properties at any temperature, but has become more or less rigid through a progressive increase in its viscosity.” In 1976, J. Wong and C. Austen Angell [11] reported on the definition proposed by a committee of the US National Research Council: “Glass is an X-ray amorphous material that exhibits the glass transition. This being defined as that phenomenon in which a solid amorphous phase exhibits with changing temperature (heating) a more or less sudden change in its derivative thermodynamic properties such as heat capacity and expansion coefficient, from crystal-like to liquid-like values.” In that same year, Eduardo Mari [12] defined glasses as “amorphous solids that are obtained by fast cooling a molten mass averting its crystallization.” A few years later, in 1982, Jerzy Zarzycki [13] defined glass as “a non-crystalline solid that presents the phenomenon of glass transition.” In 2002, K. J. Rao [14] defined glass as “a solid obtained by supercooling a liquid and that is X-ray amorphous.” In the second edition of their book, in 2013, Ivan S. Gutzow and Juern W. Schmelzer [15] proposed a longer definition: “Glasses are thermodynamically non-equilibrium kinetically stabilized amorphous solids, in which the molecular disorder and the thermodynamic properties corresponding to the state of the respective under-cooled melt at a temperature T^* are frozen-in. Hereby T^* differs from the actual temperature T .” Finally, Arun K. Varshneya’s [16–17] definition is: “Glass is a solid having a non-crystalline structure, which continuously converts to a liquid upon heating.”

2.2. Other definitions of glass

In online dictionaries and encyclopedias, one finds, among several others, the following definitions for glass:

- Merriam-Webster: “Any of various amorphous materials formed from a melt by cooling to rigidity without crystallization”
- Dictionary.com: “A hard, brittle, non-crystalline, more or less transparent substance produced by fusion”
- English Oxford Living Dictionary: “A hard, brittle substance, typically transparent or translucent, made by fusing... and cooling rapidly”
- Wikipedia: “The term glass is often defined in a broader sense, encompassing every solid that possesses a non-crystalline (that is, amorphous) structure at the atomic scale and that exhibits a glass transition when heated towards the liquid state”.

2.3. Quantitative definition of glass

All the above definitions are qualitative. At least one quantitative definition of glass was proposed in 1975 by Alfred R. Cooper and Prabhat K. Gupta [18]: “Glass is an isotropic material with relaxation time $\gg 10^3$ s and $\chi \sim 1$ ”. χ was defined as a normalized correlation

range, which is zero for a dilute gas and close to 1 for a normal liquid or a glass. The authors declared that this parameter allows a sharp distinction between polycrystalline and non-crystalline materials.

2.4. Perspective on glass definitions

As a result of several developments throughout the years [1] and taking into account that glasses (i) are not necessarily made by melting and quenching a liquid, i.e., other routes exist and are often used, such as various chemical and sol-gel techniques to produce glasses at relatively low temperatures; and (ii) not all glasses are isotropic (e.g., phosphate glass fibers and ion-exchanged glasses), a current well-accepted definition of glass is: “Glass is a non-crystalline solid that exhibits a glass transition.” One problem with this definition is that one still has to define the meaning of the glass transition phenomenon. The beauty of Varshneya’s definition [16–17] (“a solid having a non-crystalline structure, which continuously converts to a liquid upon heating”) is that it avoids the need to subsequently define the meaning of the glass transition.

Most, but not all, of these definitions and many other versions proposed in the past few decades describe glasses as being solids, and this concept has gained widespread use in the glass community, as well as the broader materials science, physics, and chemistry communities. Our overall critique about these definitions is that:

- The structure of glass is similar to that of its parent SCL;
- Glasses seem solid on a typical human time scale, but they will flow at any temperature under the action of gravity [19–22].
- The ultimate fate of glass, upon sufficiently long thermal treatments or in the limit of infinitely long time, has not been fully discussed so far. We will provide some reasoning that suggests that glasses will ultimately crystallize (solidify).

We will explore and clarify these three concepts in this communication. But let us first review the main concepts used to define “glass.”

3. Definition of key terms

- **Glass Transition Temperature, T_g :** 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, τ_R , of the supercooled liquid; $t_{\text{obs}} \sim \tau_R$. According to Maxwell’s relation, $\tau_R = \eta(T)/G_0$, where η is the equilibrium viscosity and G_0 is the infinite frequency shear modulus, which barely changes with temperature. Hence, at T_g the τ_R/t_{obs} ratio (the well-known Deborah number [23]) is unity. The structural relaxation time strongly depends on the material’s composition and the temperature. For typical oxide glasses in classical laboratory experiments by, e.g., differential scanning calorimetry (DSC) or dilatometry, carried out at 5–20 K/min, $\eta(T_g) \sim 10^{12}$ Pa·s and $G_0 \sim 3 \cdot 10^{10}$ Pa, hence, $\tau_R \sim 30$ s [24–25].
- **Solid:** The solid is a state of condensed matter where the atomic structure is thermodynamically stable and the chemical forces are strong enough to keep that structure cohesive even when it is not confined in a receptacle. Solids can be crystalline or amorphous. In a classical paper on the definition of solid and fluid [26], Alfred C. Lane stated, “A fluid has a temperature such that its plastic yield point is reached even at zero pressure.” A substance is in the solid state when its atomic configuration is time independent. A solid only flows (plastically) if a critical yield stress (Y_S), which is larger than the gravity and depends inversely on the temperature, is externally applied.
- **Liquid:** A liquid is a fluid, condensed state of matter that exhibits viscous flow. A liquid will not retain its shape, but rather flow under the forces of gravity until the shape conforms to that of the container that it occupies.
- **Supercooled Liquid:** Supercooled liquids are liquids that exist

between the melting point and the glass transition temperature. They are metastable, i.e., a thermodynamic barrier must be overcome for crystal nucleation to take place, and they relax and crystallize at any positive temperature after a certain time, which strongly depends on their chemical composition and temperature.

- **Crystal:** A crystal is a solid material having a well-ordered atomic structure on a periodic lattice. Crystalline materials may be composed of a single crystal, or they may be polycrystalline.
- **Non-Crystalline:** A non-crystalline material lacks the long-range atomic and molecular periodic order characteristic of a crystal. As first pointed out in the pioneering work of Zachariasen [27] in 1932, the glass “network is not periodic and symmetrical as in crystals. Yet it is not entirely random due to the fact that the internuclear distances do not sink below a given minimum value.” This is now a very well-known concept and needs no further explanation.
- **Amorphous:** An amorphous material has a non-crystalline structure, which differs from that of its parent liquid and does not undergo the glass transition when heated. Please note that here we draw an important distinction between glasses and amorphous solids, a point that is confused in many of the previous definitions of glass. Both glasses and amorphous solids are examples of *non-crystalline* materials, but *glasses exhibit a glass transition and amorphous solids do not*. Amorphous solids cannot be made by quenching from the liquid state, since this would result in a glass transition and hence a glass. Amorphous solids can be produced through other means, such as high-energy milling of a crystal, high-energy radiation incidence on a crystalline material, or sputtering on a cold substrate. They will crystallize without relaxing to the supercooled liquid state when heated. These differences between glasses and amorphous solids—and the fact that they are two distinct classes of material—have been discussed in detail by Gupta [28]. We refer the reader to Gupta’s insightful paper on this topic for further details on the distinction between glasses and amorphous solids.
- **Vitreous:** From the Latin, “vitrum,” vitreous refers to the glassy state and is synonymous with “glassy.”
- **Glass Structure:** Experimental data and molecular dynamics (MD) simulations of different supercooled liquids and glasses show that their atomic structure below T_g is quite similar to that of their parent supercooled liquid just above T_g . In other words, the short and medium range orders of glasses and parent SCL are very similar. For instance, Bykov et al. [29] have shown that the percentage of Q^3 units—silicate tetrahedra with 3 bridging oxygens and one non-bridging oxygen—in Na, Li, K, and Ba disilicates changes with temperature (Fig. 3), but is quite similar just below (glass) and above T_g (SCL). The crystalline forms of these same compositions have significantly different intermediate range structures with 100% Q^3 and, obviously, different long range order.
- **Frozen:** The word “frozen” means a temporary, transitory condition of very slow movement or immobilization. Some well-known uses of

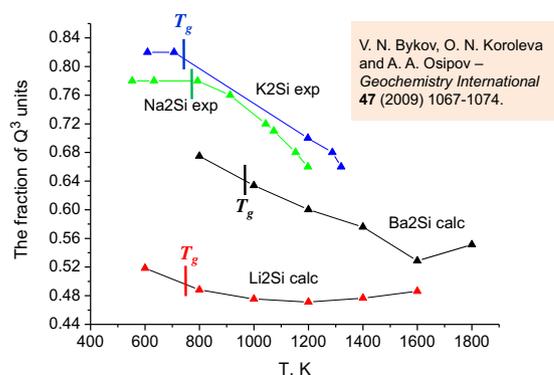


Fig. 3. Experimental and calculated fractions of Q^3 units in disilicate glasses and supercooled liquids. Figure assembled from data of ref. [25].

this term are: “frozen by fear”—a few seconds, not forever—or “frozen shoulder”—adhesive capsulitis—a frozen shoulder regains its mobility after 1–2 years. These uses of the word “frozen” bear the idea of a transitory state. This is the meaning we intend to use in the improved definition(s) of glasses to be discussed in the next session, since a glass is frozen by quenching from the liquid state, but over longer times it indeed flows and relaxes toward the supercooled liquid state. The more technical term to describe this condition of temporary freezing is “non-ergodic,” which implies that the time scale of relaxation is much longer than the observation time, i.e., a Deborah number $\gg 1$, such that the time-averaged properties of the material are different from the ensemble-averaged properties [30–32]. For example, an ensemble average of a glass structure will show fluctuations that are absent in the corresponding time average, since the structure of glass is frozen in time but can exhibit spatial variations. A detailed analysis of time vs. ensemble averaged fluctuations in glass has been previously published by Mauro et al. [33]

- **Crystallization:** 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 and growth. Nucleation is a stochastic process, hence, after some average time τ_N (which depends on the material's chemical composition and the temperature), a crystalline nucleus will form in the SCL. After that, crystal growth spontaneously starts and the material solidifies, transforming into a polycrystalline solid. In the condition of steady-state nucleation, which is typically observed above T_g , the average nucleation time $\tau_N = (I_{st}V)^{-1}$, where I_{st} and V were defined before. However, for very deep supercoolings ($T \ll T_g$), where the nucleation induction times, t_{ind} , are significant, they must be added to $(I_{st}V)^{-1}$, hence $\tau_N \leq (I_{st}V)^{-1} + t_{ind}$ [34]. Hence, to estimate τ_N at very deep supercoolings, one has to extrapolate experimental values of steady-state nucleation rates and nucleation induction times, which are normally 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 (i.e., solidify)!

4. A modern definition of glass

Having discussed the above concepts, figures, states of matter, and definitions of some key terms, and realizing that:

- The glass structures are very similar to those of their parent supercooled liquids [29].
- Glass articles do not retain their shape over a long time scale, i.e., they spontaneously start to relax and flow toward the SCL even at very low temperatures ($t_{obs} < \tau_r$). They appear to be solid indeed, and even ring, resonate, and break as if they were solids, but they do not stop flowing until they wet their substrate (or crystallize, solidify). For instance, a typical soda-lime-silica window glass ($T_g \sim 550^\circ\text{C}$) relaxes in geological time scales [19] at room temperature, whereas some organic glasses ($T_g \sim 20\text{--}50^\circ\text{C}$) relax in only a few hours;
- Glasses relax and then crystallize upon continuous heating at any temperature above absolute zero. Or they can even crystallize before complete relaxation, depending on whether T_{KS} is above or below the temperature of study;

This unique combination of properties of glasses is much more akin to those of a (supercooled) liquid than to the properties of a true solid. But at human time scales, they also exhibit hardness, elasticity, and even break (fracture) as solids. Hence, we can reasonably associate glasses with “frozen liquids” (i.e., liquids where ergodicity has been broken [31–32]) or even define them as a unique nonequilibrium state of matter. It is with these thoughts in mind that we propose an improved definition of glass.

Fig. 4 illustrates that a crystalline material (solid) will keep its internal structure and external configuration even at infinitely long time scales (a, d). At very low temperatures (say $T < 0.2T_m$), in the absence of external pressure, only under the action of gravity, a crystal may still experience some individual atomic diffusion and minor accommodation (similar to beta-relaxation in glasses and supercooled liquids) due to local rearrangement of their vacancies and dislocations, but the material retains its original atomic structure and external shape, perhaps with minor distortion. This behavior is widely different from

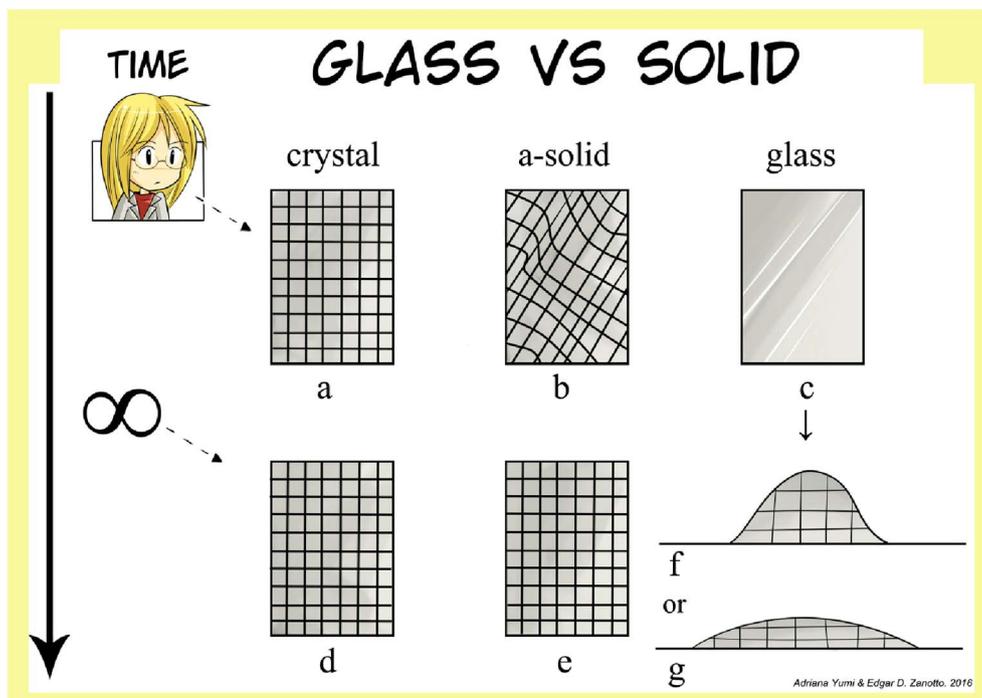


Fig. 4. Cartoon of a crystal (solid), an amorphous solid, and a glass at human time scale and their ultimate fates at an infinite time scale.

the cooperative atomic movement of many atoms in the sample that leads to structural relaxation and viscous flow of glasses and supercooled liquids. The atomic structures of crystalline solids are already configured in a thermodynamically stable arrangement; other configurations are not available for the same energetic state. They must be subjected to a critical yield stress (Y_S) before any plastic deformation or creep takes place. The value of Y_S increases with decreasing temperature and is always larger than the force of gravity. Hence crystalline materials are true solids that do not deform plastically at low temperatures under the gravity. In addition, even at sufficiently low temperatures, an amorphous solid may be able to recrystallize via atomic diffusion at a sufficiently long time scale, but it will not exhibit viscous flow (b, e).

Glasses, on the other hand, will not stop relaxing and flowing until they wet the substrate, i.e., until an equilibrium wetting angle, which is determined by the liquid/solid and liquid/atmosphere interfacial energies, is reached. And upon continuous heating, or at infinitely long times at any $T > 0$, all glasses eventually crystallize (either before (4f) or after (4g) full relaxation), as shown in Fig. 4c, f, g.

Therefore, despite some uncertainty embedded in the above discussion, some ideas are clear: the atomic structures of glasses are very similar to those of their parent supercooled liquids; and at any temperature, glasses spontaneously relax, flow, and deform under the influence of gravity. Finally, for infinitely long times, at $T > 0$ they will crystallize. Above the kinetic spinodal temperature, $T > T_{KS}$, supercooled liquids relax and then crystallize upon longer times (Fig. 4g), whereas for $T < T_{KS}$, supercooled liquids crystallize before full relaxation (Fig. 4f). Their ultimate fate is thus to transform into crystalline materials, i.e., to solidify!

As early as in 1927, Franz Simon [35] came up with the following definition of glass: “Glass is a rigid material obtained from freezing-in a supercooled liquid in a narrow temperature range.” It is not clear if he intended to convey the same meaning we are using here (frozen = a temporary state), but to make justice to that pioneer researcher, we refer to his paper [35].

Some of the greatest insight can come from an artist's perspective. According to Dale Chihuly and Sarah Bremser [36], “Glass is indeed a complex substance, with seemingly contradictory properties: ephemeral and eternal, clear and opaque, decorative and functional, fluid and brittle, material and immaterial, solid and liquid.” From a scientific point of view, glass can be seen as a special state of matter that shows the properties of solids at human time scales, but their non-crystalline structures, flow, and crystallization behaviors make them more akin to non-equilibrium frozen liquids!

From an analysis of the above discussed concepts, our proposal for an improved definition is: “**Glass is a nonequilibrium, 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 and young students.

An alternative, more elaborate description that clarifies the general properties of glasses is: “**Glass is a nonequilibrium, 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 is for those who understand the meaning of glass transition.

5. Conclusion

For many decades, researchers have attempted to define glass as either a liquid or, more typically, as 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 own unique characteristics. Glass certainly appears to be solid on a typical observation time scale: it has mechanical rigidity and

elasticity, and it can be scratched and even fractured, just as a solid. However, unlike a solid, a glass exhibits viscous flow and continuously relaxes toward the supercooled liquid state. This viscous flow behavior is more akin to that of the liquid state. In fact, the structure of a glass is similar to that of its corresponding supercooled liquid, which makes sense given that most glasses are formed by cooling from a melt. However, glasses also have properties that are unique to the glassy state due to their nonequilibrium and non-ergodic (frozen) nature. The properties of a glass depend not only on its composition and the current temperature and pressure, but also on the entire thermal and pressure histories experienced by the glass. Also, unlike either solids or liquids, glasses are thermodynamically unstable. Moreover, it has been previously shown that the glassy state itself cannot be expressed as any linear combination of supercooled liquid states [37–38]. The glassy state is therefore truly unique and can be classified as its own (nonequilibrium) state of matter. Our definition can also be applied to other “non-standard” types of glasses such as vitrifying liquid crystals, which are partially crystalline but have a vitreous matrix that exhibits a glass transition [39–40]. In the end, though, the existence of any glass is transient, since it will relax toward the supercooled liquid state and ultimately crystallize (solidify). We hope that the two new definitions of glass proposed in this communication will help educate and inspire the public about this beautiful and technologically transformative material and also help inspire the next generation of glass scientists, engineers and artists.

Acknowledgements

Throughout four decades of working on glass research and teaching, EDZ has been asked many times by students and colleagues of different backgrounds to explain the concept of “glass.” JCM has encountered the same experience numerous times. Hence, we made an effort to put together this article, which hopefully can be educative and useful, not only for the general public and students, but also for the scientific community. The authors are grateful to the CeRTEV (www.certev.ufscar.br) researchers for their critique and insights about the above described concepts, and to Joachim Deubener for suggesting and translating from German some classical references, and also for his useful comments. Profs. A. Varshneya, A. C.M.Rodrigues, E. B. Ferreira and M. L. F. Nascimento made relevant suggestions. Daniel R. Cassar helped us in producing Fig. 2. We are also grateful to Kenneth L. Burns from the Rakow Research Library at the Corning Museum of Glass for help with the Chihuly reference. Funding by the São Paulo State Foundation, FAPESP (#2013/07793-6) is deeply appreciated.

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