



## The glassy state of matter: Its definition and ultimate fate

Edgar D. Zanotto<sup>a,\*</sup>, John C. Mauro<sup>b,\*</sup>

<sup>a</sup> Department of Materials Engineering, Center for Research, Technology and Education in Vitreous Materials, Federal University of São Carlos, SP, Brazil

<sup>b</sup> Science and Technology Division, Corning Incorporated, Corning, USA

### ARTICLE INFO

#### Keywords:

Glass  
Thermodynamics  
Kinetics  
Glass transition  
Relaxation  
Crystallization

### 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 is to solidify, i.e., crystallize.” This definition is for advanced students 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 6000 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,  $\tau_R$ . 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 short, medium and long range, which are thermodynamically stable

\* Corresponding authors.

E-mail addresses: [dedz@ufscar.br](mailto:dedz@ufscar.br) (E.D. Zanotto), [mauroj@corning.com](mailto:mauroj@corning.com) (J.C. Mauro).

<http://dx.doi.org/10.1016/j.jnoncrysol.2017.05.019>

Received 2 March 2017; Received in revised form 27 April 2017; Accepted 15 May 2017  
0022-3093/ © 2017 Elsevier B.V. All rights reserved.

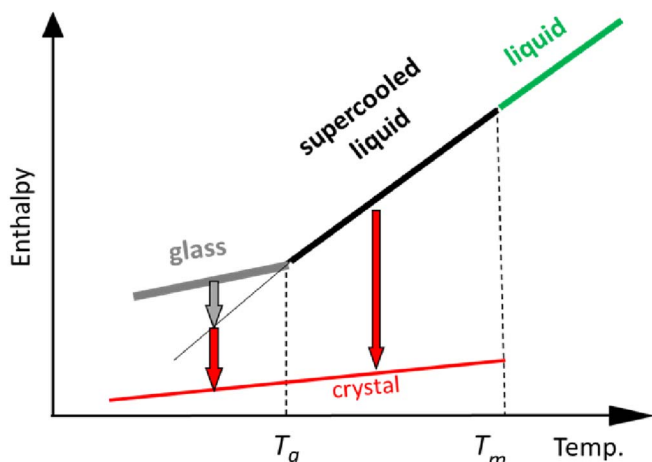


Fig. 1. Schematic enthalpy versus temperature plot for a glass-forming substance showing four distinct states: liquid (L), supercooled liquid (SCL), glass (G), and crystal (C).  $T_m$  = melting point or liquidus temperature,  $T_g$  = glass transition temperature. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

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,  $\tau_R$ , of the supercooled liquid is equal to the average time required to form the first critical crystalline nucleus in the supercooled liquid,  $\tau_N$  ( $\tau_N = (I_{st}V)^{-1}$ , 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

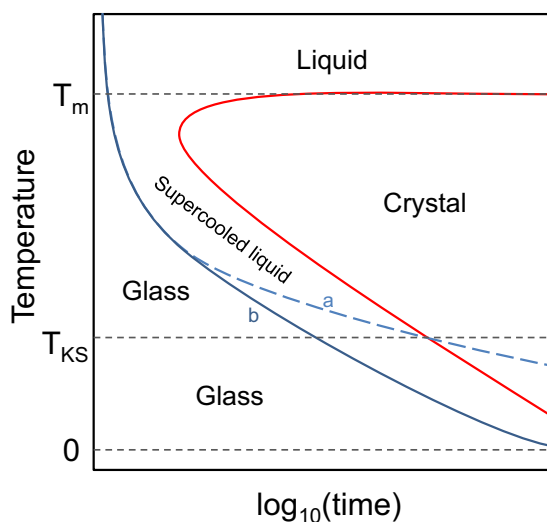


Fig. 2. Schematic representation of the average structural relaxation time of a supercooled liquid,  $\tau_R$  (blue curves a and b) and the average nucleation time,  $\tau_N$  (red line) as a function of the temperature.  $T_{KS}$  is the kinetic spinodal temperature. In path a, the average relaxation times curve of a supercooled liquid (dashed blue line) cross the crystal nucleation times curve at  $T_{KS}$ , whereas in path b (blue line), they never cross. Both paths are theoretically possible. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

average relaxation time curve of a supercooled liquid (blue line) crosses the crystal nucleation time curve (green line) at  $T_{KS}$ , whereas in path b (blue circles), 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 the 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, Jerzi 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  $\chi \sim 1$ ”.  $\chi$  was defined as a normalized correlation

Download English Version:

<https://daneshyari.com/en/article/5441122>

Download Persian Version:

<https://daneshyari.com/article/5441122>

[Daneshyari.com](https://daneshyari.com)