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The glass, the glassy state and the Alice number¹

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Abstract

In the present contribution a critical discussion is made, on the basis of the different definitions of the terms *glass* and *glassy state*. Some new refined versions of these definitions are proposed. Special attention is paid to the characterisation of the kinetic frozen state. A new freezing-in criterion, proposed to be called *Alice number* is introduced. This criterion is used to characterise the kinetic freezing process as well as the kinetic frozen state.

Keywords: Glass; Glassy state; Kinetic freezing criteria

1. Introduction

Recently the terminology concerning glass and the glassy (vitreous) state is still in a process of development and refinement. This is instead of the existence of established scientific concepts in this area. The difficulty is to include these concepts into exact formulations.

In the present contribution a critical discussion will be made, based on the different definitions of the terms *glass* and *glassy state*. Some new refined versions of these definitions will be proposed. Special attention will be paid to the characterisation of the kinetic frozen state. A new freezing-in criterion, proposed to be called *Alice number* will be introduced. This criterion will be used to characterise the kinetic freezing process as well as the kinetic frozen state.

The present author admits that scientific terms and definitions do not reflect only scientific reality; they are also a form of scientific agreement. Therefore the definitions proposed below have to be regarded as announcement, aimed at such an agreement.

¹ Dedicated to Professor Hiroshi Suga.

2. On the definitions of *glass* and *glassy state*

2.1. A detailed analysis

Many definitions of the terms *glass* and *glassy state* have been proposed and broadly used (see, for example, Refs. [1–7]). From these definitions some important features of the glass and of the glassy state can be extracted. These features are presented below, conditionally separated into two parts: 1—less debatable; and 2—more debatable.

2.1.1. Some relatively established views on glass and the glassy state

2.1.1.1. *The glassy state is a non-equilibrium, kinetic frozen state.* The statement 2.1.1.1 is, in general, accepted. However, some theoretical speculations have been made about the existence of an ‘ideal’ metastable glassy state which can not be reached because of kinetic reasons only. If this is the case, then a hypothetical second range phase transition must occur between a metastable liquid state (undercooled liquid) and an ‘ideal’ glassy state (fully relaxed glass). At present this concept is not proved empirically and therefore its heuristic value is doubtful (see Refs. [1, 8]).

2.1.1.2. *Glass is in a glassy state.* This statement is of course unquestionable. However, this is no case for the stronger statement: all materials and systems in glassy state are glasses. The latter will be discussed in Section 2.1.2.2.

2.1.1.3. *The terms ‘solid’ and ‘solidification’ are not definitive for a glass and a glass transition.* In some earlier works a glass has been defined as a solid and the glass transition as a process of solidification [3, 5]. The recent viewpoint is that the glass transition is a kinetic phenomenon (see Refs. [1, 8, 9]). In the glass transition region the structure of the liquid freezes-in. The dramatic rise of the viscosity is only one of the (important) consequences of this kinetic freezing.

2.1.1.4. *Glass is a material without restriction on its chemical composition.* Glasses with different chemical compositions like oxide, halide, metallic, organic, etc. content are well known. Some attempts have been made [3, 4] to exclude organic materials from the definition of glass but this is not widely accepted.

2.1.1.5. *The glass structure is amorphous.* A lack of translational symmetry is characteristic of the structure of most materials defined as glasses. However, an interesting proposal has been made to call *glassy crystals* materials obtained by kinetic freezing of some stable or metastable crystals [10, 11]. It must be pointed out that even in this case some kind of positional or orientational disorder is essential [10].

2.1.2. Disputable views on glass and glassy state

2.1.2.1. *Glass can be obtained only by kinetic freezing of a liquid phase.* Following the ideas of Gustaw Tammann (see Ref. [12]), most scientists agree with this statement [1–6]. On the other hand, materials like *spin glasses* [13], *gel glasses* [14], *glassy*

crystals [10], etc., obtained not from a liquid phase, pretend to be glasses too. A discussion on this problem will be made in Section 2.1.1.2.

2.1.2.1.1. *After kinetic refreezing of a glass, on passing a glass transition interval the precursor liquid has to be restored.* This is an alternative formulation of the requirement 2.1.2.1. It looks as if there is some difference between 2.1.2.1 and 2.1.2.1.1 only for materials with a very high crystallisation tendency. It is difficult, for example, to study the glass transition of a metallic glass with a conventional calorimeter, because the heating rates available are relatively low. In this case crystallisation occurs before the liquid state can be reached. This, however, is not a principal limitation [15]. In fact, it is easier to realise fast heating than fast cooling. For fast heating different pulse techniques (electric, laser, electron, etc.) can be used. One can imagine a new type of a pulsed calorimeter to study the glass transition in fast-crystallising glasses. The problems here are more mathematical and technical rather than physical.

2.1.2.2. *Not all materials in a glassy state are glasses (See also 2.1.1.2).* At present this statement is not generally accepted. Despite this an attempt will be made here to maintain its usefulness. On this purpose *the rule of contrariers* will be applied: let us for the first time suppose that all materials in a glassy state are glasses. Then there are two possibilities.

- (1) The statement 2.1.2.1 is accepted [1, 5, 6], in which case the application field of the term *glassy state* becomes too small and covers only the states of the frozen-in liquids.
- (2) The statement 2.1.2.1 is not accepted [10, 11], in which case some materials like *gel glasses, spin glasses, glassy crystals* etc., mentioned above, can be defined as glasses and the application field of the term *glass* becomes too extensive.

The supporters of the first possibility lay emphasis on the differences in the thermodynamic and kinetic description of the different frozen-in systems. The supporters of the second possibility, contrariwise, emphasise the similarities in this description.

Both of these theses have their scientific reasons: on one hand in (2) the state of all kinetic frozen systems is non-equilibrium and principally can be described in the framework of the thermodynamics of irreversible processes. On the other hand in (1) for a full characterisation of a non-equilibrium state one or more internal parameters are necessary. These internal parameters depend on the prehistory of the state. Consequently the states of different frozen-in systems, obtained by qualitatively different methods, are described generally by different sets of internal parameters. As a result these states must also be qualitatively different.

The supporters of thesis (1) are mostly glass scientists; the supporters of thesis (2) maintain a viewpoint, preferably thermodynamic in its nature. Who is right?

It is believed here that the answer to the last question has to be based on scientific agreement, rather than scientific argument. One way for such a compromise agreement is the acceptance of the statement 2.1.2.2.

Let us now suppose that not all materials and systems in the glassy state are glasses. Then the term *glass* can be preserved in its classical, ‘restricted’ meaning (2.1.2.1) for materials science. On the other hand the term *glassy state* can be regarded in a ‘broader’ thermodynamic sense. Now the state of the *gel glasses*, *spin glasses* etc. can be depicted as ‘glassy’. These materials are glass-like, but they are not glasses. They have its specific sets of internal parameters and its corresponding specific properties.

2.2. *New formulations*

Some new formulations of the definitions of glass and the glassy state can be proposed in accordance with the features discussed above 2.1.1.1–2.1.1.5, and 2.1.2.1 and 2.1.2.2.

2.2.1. *Definition 1: A glass is a material with frozen-in liquid-like structure*

This definition is a modified variant of the classical definition ‘a glass is a frozen-in liquid’. The only difference is that here an attempt has been made to unload the rich enough term *liquid* with the term *glass* [16]. The aim is to emphasise the difference between the state of a liquid, which is equilibrium, and the state of a glass, which is essentially in non-equilibrium [1].

2.2.2. *Definition 2: A glassy state is a frozen-in state of a disordered system*

This definition is very broad and incorporates the kinetic frozen states of different materials (e.g. glasses, gel glasses) as well as material subsystems (e.g. spin glasses). The only restriction which has been made is that these materials must have a disordered structure. What must be understood here is the lack of translational symmetry. This restriction is required in order to distinguish the term *glassy state* from the terms *kinetic frozen state (frozen-in state)* (see 2.1.1.5).

In this connection definitions of some other materials and material subsystems can be proposed.

2.2.3. *Definition 3: A gel-glass is a material with frozen-in gel-like structure*

2.2.4. *Definition 4: A spin-glass is a frozen-in disordered spin system in diluted magnetic alloys*

As is apparent one of the major questions arising with respect to the definitions just proposed, is: “What does ‘frozen-in state mean?’” The answer to this question will be discussed in the next section.

3. **Kinetic freezing criteria**

3.1. *Present-day kinetic freezing criteria*

Let us, for simplicity, describe the relaxation of a system in relation to its thermodynamic equilibrium by a first order kinetic differential equation for only one

internal parameter ξ :

$$\frac{d\xi}{dt} = -\frac{\Delta\xi}{\tau} \quad (1)$$

Here $\Delta\xi$ is the displacement of ξ from its equilibrium value and τ is the relaxation time. Then the mathematical condition for kinetic freezing can be expressed as follows:

$$\frac{d\xi}{dt} = 0 \quad (2)$$

Since $\Delta\xi \neq 0$ (the system is not in equilibrium), then the condition (2) is equivalent to the condition $\tau \rightarrow \infty$. In the case of an Arrhenius temperature-dependence of the relaxation time

$$\tau(T) = \tau_0 \exp\left(\frac{E}{kT}\right) \quad (3)$$

condition (2) can be realised only when $T \rightarrow 0$. In all real cases the relaxation velocity has a finite quantity and the mathematical freezing-in condition (2) cannot be satisfied.

It was Reiner who first mentioned the need to introduce a physical kinetic freezing condition. For the purpose of distinguishing solids from fluids, he proposed a dimensionless criterion—the Deborah number, DN :

$$DN = \frac{\tau}{\theta} \quad (4)$$

Here θ is a reference time, called time of observation [17].

Reiner argues his choice for the name of the new freezing-in criterion with the prophetess Deborah's words: 'The mountains flowed before the Lord'. According to Reiner, the prophetess knew two things: 'First, that the mountains flow, as everything flows. But, secondly, that they flowed before the Lord, and not before the man, for the simple reason that man in his short lifetime cannot see them flowing, while the time of observation of God is infinite' [17].

Besides the Deborah number, some other physical criteria for kinetic freezing are also known. If, for example, the glass transition is described in the framework of the Tool–Narayanaswamy model [18, 19], then the upper, T_u , and the lower, T_l , limits of the glass transition region can be defined using the temperature derivative of the fictive temperature, T_f :

$$\left[\frac{dT_f}{dT}\right]_{T=T_u} = 1 - \varepsilon \quad (5a)$$

$$\left[\frac{dT_f}{dT}\right]_{T=T_l} = \varepsilon \quad (5b)$$

Here ε is a small number [20].

Another freezing-in criterion, the Lillie number [21], Li , was introduced by Cooper and Gupta using the time derivative of the relaxation time [20]:

$$Li = \frac{d\tau}{dt} \quad (6)$$

A similar criterion for glass transition has been proposed by Wolkenstein and Ptitzin [9]:

$$\left[\frac{d|q\tau|}{dT} \right]_{T=T_g} = -1 \quad (7)$$

Here $q = (dT/dt) < 0$ is the cooling rate and T_g is the glass transition temperature. If the cooling rate is constant and the temperature-dependence of the relaxation time is of an Arrhenius type (Eq. (3)), condition (7) leads to condition (6).

The physical freezing-in criteria just mentioned are useful, but they show also a lack of universality. The Deborah number is intended to characterise a kinetic frozen state and the other criteria—a kinetic freezing process. Moreover, the criteria do not contain explicit information about the deviation from equilibrium which is also responsible for the relaxation kinetics (see Eq. (1)). A new physical kinetic freezing criterion has to be introduced to avoid these shortcomings.

3.2. The Alice number

A natural kinetic freezing criterion, the Alice number, AN , can be proposed [16]:

$$AN \equiv \frac{V_{\text{actual}}}{V_{\text{ref}}} \quad (8)$$

Here $V_{\text{actual}} = d\xi/dt$ is the actual relaxation velocity and V_{ref} is a reference one. The Alice number, now, is able to characterise a kinetic freezing process as well as a kinetic frozen state when adequate reference relaxation velocities, V_{ref} , have been chosen.

3.2.1. The Alice number and the kinetic freezing process

Let us regard an equilibrium system initially in isobaric condition which is cooled down with a velocity q . Let this cooling rate be fast enough to avoid any possible first-order phase transitions. In this case on passing a kinetic freezing interval the system becomes kinetically frozen as a consequence of the sudden rise of the relaxation time (see Eq. (3)). If the initial system is a liquid, then the final one will be a glass and the corresponding kinetic freezing is called a glass transition. In the frame of the Tool–Narayanaswamy model a generalised fictive temperature, T_f , can be used as an independent internal parameter [1]. Here the difference $\Delta T_f = T_f - T$ characterises generally the system's deviation from equilibrium. Although the generalised T_f does not have the same simple physical meaning, it is the equivalent of Tool's original fictive temperature. The actual relaxation velocity can be expressed as:

$$V_{\text{actual}} = \frac{dT_f}{dt} = q \frac{dT_f}{dT} \quad (9)$$

If now a reference relaxation velocity, $V_{\text{ref}} = q$, is chosen, then the corresponding Alice number is simply equal to the temperature derivative of the fictive temperature.

$$AN = \frac{V_{\text{actual}}}{q} = \frac{dT_f}{dT} \quad (10)$$

The kinetic freezing interval can be characterised by its upper, T_u , and lower, T_l , limits in accordance with conditions (5a) and (5b).

3.2.2. The Alice number and the kinetic frozen state

Let us regard again a simple non-equilibrium system in which relaxation is governed by the first-order kinetic equation, Eq. (1) and let the external conditions be kept constant. It follows from Eq. (1) that the actual relaxation velocity is:

$$V_{\text{actual}} = \frac{\Delta \xi}{\tau} \quad (11)$$

In this case a proper choice of the reference relaxation velocity is:

$$V_{\text{ref}} = \frac{\delta \xi}{\theta} \quad (12)$$

Here θ is the time of observation or exploitation and $\delta \xi$ designates the smallest change of the relaxed parameter ξ which can be measured, or which is of interest. The corresponding Alice number can be expressed as:

$$AN = \frac{\theta \Delta \xi}{\tau \delta \xi} = \frac{1}{DN} \frac{\Delta \xi}{\delta \xi} \quad (13)$$

It is not surprising that the Alice and Deborah numbers are reciprocal because the Alice number is a velocity criterion and the Deborah number a time one. The important difference is that the Alice number takes into consideration not only the time part of the relaxation kinetics as the Deborah number does. It contains also information about the relaxation driving force, $\Delta \xi$, and the measurement accuracy, $\delta \xi$. As a consequence, using the Alice number we can characterise the state of a system as kinetic unfrozen ($AN > 1$) even when the respective Deborah number predicts frozen-in state ($DN > 1$). This takes place when a great deviation from equilibrium occurs (great $\Delta \xi$) and/or when a high accuracy in determining ξ is available and of interest (small $\delta \xi$).

Returning to the Reiner's poetic example we can now ascertain the fact of the mountain flowing not only before the Lord, but before the man also, despite the human's short lifetime. This is because there are great mechanical stresses concentrated in the earth's crust and because great accuracy in determining mountain flow is now available thanks to the space techniques.

In the case of a Maxwell relaxation the corresponding *mechanical Alice number* can be expressed:

$$AN = \frac{\sigma}{G \delta \varepsilon} \frac{\theta}{\tau} \quad (14)$$

Here θ is the time of observation, τ is the Maxwell relaxation time, σ is the mechanical strain applied, $\delta\varepsilon$ is the accuracy in determining the mechanical stress, and G is the corresponding elastic modulus. It can be seen from Eq. (14) that for a given set of σ , τ , θ and G , the Alice number depends on the quantity $\delta\varepsilon$ also. That introduces some relativity into the determination of the Alice number because different measuring techniques are characterised with different measuring accuracy. Which method has to be taken into account? Returning to our example we can regard mountain flow (or continental drift) relative to some different cases. On the one hand if we are interested in some transportation problems (for example, a jet flying between London and New York) we will be satisfied with a relatively great error in determination of transportation distance ($\delta\varepsilon =$ several kilometres). In this case the corresponding Alice number will be small ($AN \ll 1$) and continental drift need not be taken into account. The transportation distance London to New York can be regarded as a constant. If, on the other hand, we are interested in geological problems (for example the sinking of Japan) very small continental displacements ($\delta\varepsilon =$ several millimetres) can be of essential importance. In this case the corresponding Alice number will be great ($AN > 1$) and mountain flow has to be considered. Consequently the proper choice of Alice number in a given specific case is made not only on the basis of physical and technical considerations. Utilitarian reasons also must be taken into consideration.

4. Conclusion

At present concepts concerning glasses and the glassy state are well established, although there are two different views about the extension of the field of application of these terms. The first, which originates from classical glass science, prefers to define as glasses only materials obtained by kinetic freezing of a liquid phase. The second, which is more connected with thermodynamics, prefers to extend the field of application of the term glassy (or vitreous) state to the states of all systems with kinetically frozen structural disorder.

It has been shown in the present work that this contradiction can be avoided if the statement 2.1.2.2. 'Not all materials in a glassy state are glasses' is accepted. In this connection some new versions of the definitions of the terms *glass*, *glassy state*, *gel glass* and *spin glass* have been proposed.

A new freezing-in criterion, the Alice number, has been used in order to characterise the kinetic freezing process as well as the kinetic frozen state. This characterisation is relative to a reference relaxation velocity, V_{ref} . The latest has to be chosen on physical, technical and/or utilitarian reasons.

The name of the Lewis Carroll's character, Alice, is chosen for the new criterion in order to lay emphasis on this relativity. And it is well known that many children (i.e. young scientists) are introduced to the phenomenon of relativity with the wise help of the Alice's stories.

Despite the relativity which is essential in the characterisation of the freezing-in process and the frozen-in state, it must not also be regarded as being arbitrary. There are some rules in selection of V_{ref} (see above). Moreover, for a given type of material (for

example, window, thermometric or optical glasses) some standard values can be taken for V_{ref} [22]. Then, with reference to these standard values one can say for the state of a system 'it is frozen-in' and not only 'it may be regarded as frozen-in'.

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