



Perspective: Thermodynamics of structural glasses



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ARTICLE INFO

Article history:

Received 6 June 2014

Received in revised form 24 June 2014

Available online 17 July 2014

Keywords:

Thermodynamics;

Glass transition;

Broken-ergodicity;

Residual entropy;

Free energy

ABSTRACT

According to the conventional wisdom, a (liquid to) glass transition takes place when a liquid, upon cooling, falls out of equilibrium because the observation time becomes less than the structural relaxation time of the liquid. The external time constraint prevents the system from exploring its entire configurational space. The freezing of the slow configurational changes that occur on a time scale longer than the observation time partitions the configurational space into mutually inaccessible components and the system becomes trapped in each component of the partition with a probability that is equal to the probability with which it was exploring that component before partitioning. A glass is such a broken-ergodic system. The volume of the configurational space accessible to a glass is reduced resulting in a loss of configurational entropy during a glass transition. This view of a real glass transition, called the disordered solid (or the broken-ergodic) view, is consistent with all observed features of glass transition such as absence of latent heat and a drop in the heat capacity. Thermodynamics of glassy state based on this and the traditional view are compared. It is concluded that the broken-ergodic view is fundamentally sound but not the traditional view.

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1. Introduction

The ‘far from equilibrium’ nature of the glassy state poses serious questions about the thermodynamics of glasses and of glass transition. These range from ‘how to define entropy of such a non-equilibrium state?’ to ‘what is the nature of the glassy state?’ to ‘must glasses have a positive residual entropy (entropy at $T = 0$ K)?’. There are no widely agreed upon answers and the issues remain (and have been for a long time) mired in deep controversies. This paper provides a perspective from the point of view of a physics-oriented materials scientist with primary interest in the science and engineering of inorganic glasses. In the past couple of decades, the ‘disordered state physics’ community has witnessed new theoretical developments [1–3], rigorous microscopic models [4,5], and extensive insights based on atomistic simulations [6, 7] and it is comforting to note that many key concepts traditionally used in glass science and engineering (e.g., the notion of fictive temperature as an additional state variable for characterizing the history dependence of properties of glasses) have been placed on a more solid statistical mechanical foundation.

There exist, in the current literature, a wide variety of glasses: spin glasses [8–10], granular glasses [11,12], colloidal glasses [13], glassy crystals [14], and structural glasses [15–17] which have been investigated by experiments, theory, and simulations [18]. Structural glasses include the conventional liquid-cooled glasses as well as amorphous solids made by processes other than cooling a liquid (e.g., vapor deposition or solid state amorphization). The focus of this paper is on

conventional liquid-cooled structural glasses. In the following, the term ‘glass’ is used to refer to these glasses. In addition, the term ‘liquid’ is used to include super-cooled liquids. Also, it will be assumed that the time scale of crystallization is much larger than any other time scale of relevance to glassy state.

While the term glass transition is always used to describe the transformation of a liquid into a glass upon cooling, it is, sometimes, also used for the inverse process where, upon heating, a glass converts to the liquid [19,20]. In this paper, these two processes are distinguished because of the non-equilibrium nature of glass. The term ‘glass transition’ is used strictly for the liquid to glass transformation. The process where a glass transforms to liquid is referred to as ‘relaxation’.

There are (at least) two camps of thought about the nature of glass transition. Many (though not all) theoreticians [21,22] focus on the ‘ideal (also called thermodynamic or equilibrium) glass transition’ that hypothetically takes place at the Kauzmann temperature [23] if a liquid is somehow continued to low enough temperatures. Others (myself included) are concerned primarily with the real (i.e., kinetic) glass transition in which a liquid falls out of equilibrium during cooling as a result of the observation time scale (to- inverse of the cooling rate) becoming less than the (average) structural relaxation time, $\tau(T)$, in the liquid. The discussion in this paper is limited to real glasses made by kinetic glass transition that, in the following, is simply referred to as glass transition.

For a kinetic glass transition, it is natural to define a glass transition temperature, T_g , by the following equation:

$$\tau(T_g) = t_0. \quad (1)$$

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T_f is also called effective, internal, configurational, or fictive temperature. The term ‘fictive temperature’ is used in this paper following Tool [24] who first introduced the concept. The fictive temperature, in principle, depends on other external variables such as volume and composition. These variables are considered fixed and are not shown explicitly in the rest of this paper.

For a given T_f , Eq. (1) suggests that glass formation can be thought of as a sequence of three steps:

- i) A liquid is brought quasi-statically from some initial temperature to T_f . A quasi-static process is one for which the observation time is large so that a system remains in equilibrium at all times:

$$\tau(T \geq T_f) \ll t_0^{qs}. \tag{2}$$

- ii) At T_f , t_0 is switched to a lower value, t_0^{iso} , such that

$$\tau_{vib} \ll t_0^{iso} \ll \tau(T \leq T_f). \tag{3}$$

This externally imposed time-constraint induces glass transition to take place at T_f by freezing the (slow) configurational degrees of freedom.

- iii) The glass is brought from T_f to the desired T by a fast iso-structural process (corresponding to t_0^{iso}) in which no configurational changes take place while the vibrational degrees of freedom remain in equilibrium with the thermal bath. The state of the glass is then specified by two temperatures: the temperature, T and the fictive temperature, T_f .

Thus by combining iso-structural (in the glassy regime) and quasi-static (in the liquid regime) processes with the thermodynamics of glass transition, it is possible to a) develop the thermodynamics of a glass having a specified fictive temperature, b) connect the thermodynamics of a glass to the equilibrium thermodynamics of the liquid state, and c) connect thermodynamics of glasses having different fictive temperatures.

Because there are no configurational changes, the configurational properties (e.g., the average potential energy, E) do not change during a glass transition:

$$E(gls, T = T_f, T_f) = E(liq, T_f). \tag{4}$$

What can be said about the configurational entropy change during a glass transition? The answer depends on how one defines the configurational entropy of a glass. Currently, this is a highly contentious issue [25,26]. Jackle [27] has analyzed both sides of the controversy in detail. He termed the two views of glass as the ‘quenched liquid’(QL) and the ‘disordered solid’ (DS) views. Both views treat a glass as a nonequilibrium state in which the fast vibrational degrees of freedom remain in equilibrium with the physical thermal bath of temperature (T) and the slow configurational degrees of freedom are determined by a different (fictive) thermal bath of temperature (T_f). The two views, however, differ in the manner in which the configurational entropy of a glass depends on T_f .

According to the QL view, a glass behaves configurationally like the liquid at T_f and there is no change in the configurational entropy during a glass transition:

$$S^{QL}(gls, conf, T = T_f, T_f) = S(liq, conf, T_f). \tag{5}$$

Since configurational changes are forbidden, the configurational entropy of a glass is T -independent. Eq. (5), therefore, implies a positive residual entropy for glasses:

$$S^{QL}(gls, T = 0, T_f) = S(liq, conf, T_f) > 0. \tag{6}$$

Thus, in the QL view, the third law of thermodynamics is violated (Eq. (6)) and, because of Eqs. (4) and (5), the second law is obeyed during the glass transition.

The QL view represents the conventional wisdom. It is supported by the classical phenomenology [28–30] of glassy state based on internal parameters (sometimes called order parameters in the glass community). Leuzzi and Nieuwenhuizen, in their 2008 monograph [31], discussed the thermodynamics of the QL view and referred to it as the ‘two temperature thermodynamics’ (TTT) model. The TTT model has been embraced by several other researchers [32–38].

In the DS view, while the configurational degrees of freedom in a glass remain the same as in the liquid at T_f , configurationally a glass is not identical to the liquid at T_f . In this view, freezing of the configurational degrees of freedom at T_f implies a partitioning of the configurational space, effectively trapping the representative point of a glass among various components of the partition with a probability distribution that is determined by T_f . A glass, in the DS view, is thus a broken-ergodic system and glass transition an ergodicity-breaking transition. Since the average configurational space volume available to a component is greatly reduced (compared to the volume of the entire configurational space explored by a liquid), there is a loss of configurational entropy during a glass transition:

$$S^{DS}(gls, conf, T = T_f, T_f) < S(liq, conf, T_f) \tag{7}$$

Cohen and Turnbull [39], were the first to suggest the DS view. They stated that “the glassy state is truly metastable and not unstable; consequently, by the Nernst theorem, it would have vanishing entropy at 0 K”. However, their brief communication did not receive much attention. Recently, Gupta and Mauro [40,41] have revived interest in and extended the DS view. Several others have also expressed support for the DS view [42–48].

Since at $T = 0$, each component of the configurational space reduces to a single configuration, the DS view predicts a zero residual entropy for a glass (in contradiction to Eq. (6)):

$$S^{DS}(gls, T = 0, T_f) = 0 \tag{8}$$

Thus, in the DS view, the third law is obeyed (Eq. (8)) but the second law is violated (see Eqs. (4) and (7)) during the glass transition.

Which view of glass is correct: the quenched (frozen) liquid view or the disordered solid (broken-ergodic) view? Unfortunately, there are no direct measurements of entropy. Calculations of entropy values are always based on the thermodynamic relationship, valid only for reversible processes, between entropy and heat capacity (C):

$$\left. \frac{\partial S}{\partial T} \right|_{Rev} = \frac{C}{T}. \tag{9}$$

But a glass transition is not a reversible process and application of Eq. (10) to glass transition has no thermodynamic basis.

The ergodicity-breaking nature of the glass transition is supported by the behavior during glass transition of experimentally measurable properties such as the heat capacity (C) and compressibility that are directly related to fluctuations. Both of these properties show a drop during glass transition [49,50]:

$$C(gls, T = T_f, T_f) < C(liq, T_f). \tag{10}$$

Eq. (10) is actually considered a universal signature of glass transition. Additional evidence of broken-ergodicity comes from isothermal spectroscopy measurements over a wide range of frequencies of properties like heat capacity [51,52]. Spectroscopy experiments reveal that a glass transition can also occur at a constant temperature by variation of t_0 as is expected for an ergodicity breaking transition.

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