Glass Transition ☆

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Glass transition is a term that was originally used to describe the marked changes in thermodynamic derivative properties, such as heat capacity and thermal expansivity, that usually accompany the solidification of a viscous liquid during cooling (or sometimes compression). In recent times, however, it has become more broadly applied to describe any phenomenon that is caused by a timescale (on which some interesting degree of freedom equilibrates) becoming longer than the timescale on which the system is being observed. This is because nowadays there are many different sorts of "glasses" under discussion (Angell, 1995; Palmer et al., 1985; Loidl et al., 1991; Tadic et al., 1988; Natterman and Scheidl, 2000).

The general concept of "glass" relates to systems that have some degree of freedom that:

1. Fluctuates at a rate that depends strongly on temperature or pressure; and
2. becomes so slow at low T or high P that the fluctuations become frozen to ordinary timescale measurements.

At this point, properties determined by the fluctuation of the slow degree of freedom change value more or less abruptly, giving the "glass transition." For instance, in spin glasses, it is the magnetic susceptibility that decreases suddenly as the fluctuations in magnetization freeze in, while with glass-forming liquids, it is the heat capacity, compressibility, expansivity, and dielectric susceptibility. Thus the most general definition can be given for a "glass" is: "a glass is a condensed state of matter, which has become 'nonergodic,' (see Palmer et al., 1985) by virtue of the continuous slow down of one or more of its degrees of freedom." As commonly stated, the system has "fallen out of equilibrium." Satisfying this definition, there are spin glasses (Palmer et al., 1985) and orientational glasses (dipole, quadrupole, octapole) (Kim et al., 2000; Loidl et al., 1991; Tadic et al., 1988) and vortex glasses (Natterman and Scheidl, 2000), as well as the classical glasses, which themselves have now become known as "structural" glasses. Even ordinary crystals can be considered "glasses" by this definition. This is because when defect concentrations become frozen-in during cooling, there is a quite sudden change in certain properties. For instance, the temperature dependence of electrical conductivity of ionic crystals undergoes a sudden jump when the defect concentration unfreezes during heating. While this is a simple case, as far as visualizing the degree of freedom (the defect population) is concerned, it is in fact atypical because the "freezing-in temperature" may depend on the crystal size. For lattice vacancy defects, for instance, changes in defect population require migration of defects to or from the crystal surface, which can be slow. In the glasses that are getting the most attention today, the timescale for establishing equilibrium is intrinsic to the substance, provided that the samples are large enough for surface layer effects to be negligible. This is because the "defects" or "structural states" are generated internally.

"Structural" glasses are distinguished from most others by the large change in heat capacity (thermal susceptibility), which accompanies the freezing-in of a particular structural state, or defect, population. Consequently, the Kauzmann paradox, to which so much attention has been given in structural glass studies, is not discussed in other glass physics circles. Among structural glasses, the only cases that lack the heat capacity jump are those at the "strong" extreme of the overall strong/fragile behavior pattern (see below), and these have been considered the least interesting (at least until recently when "polymorphism" in strong liquids became recognized (Angell et al., 1994; Mishima, 1994)). The importance of the heat capacity jump in the phenomenology of "structural" glasses, and the importance of the equilibrated state being kinetically stable enough to study and characterize, are both included in the definition of a "structural" glass preferred by this author.

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"A (structural) glass is an amorphous solid, which is capable of passing continuously into the viscous liquid state, usually, but not necessarily, accompanied by an abrupt increase in heat capacity."

Note that, until recently, this definition relegated most of the "metallic glass" materials to the gray world of "amorphous solids" because, although formed from a liquid (by ultrafast quenching), they crystallize on reheating before ever achieving the supercooled liquid state. Fortunately for the field, a number of bulk glass-forming metallic systems are now becoming known (Johnson, 2000) and their glass transitions are of familiar form. It is notable that many substances that are glass by this definition can form without ever passing through a liquid state (Angell, 1995).

When a liquid is cooled to temperatures lower than its equilibrium crystallization temperature at a rate that is rapid enough to avoid crystallization, it enters a metastable super cooled state. The dynamical behavior of super cooled liquids presents many features, such as non-exponential, multi-stage decay of fluctuations and a rapid growth of relaxation times. As the temperature is reduced further, the viscosity of the super cooled liquid becomes so high that it behaves like a disordered solid for most purposes. This state of matter is called `structural glass'. The glass transition temperature is conventionally defined as the temperature at which the viscosity reaches a value of 10^{13} P. Analytical approaches to the development of an understanding of the behavior of simple super cooled liquids near the structural glass transition are reviewed (Dasgupta, 2005).

Having properly recognized the broadness of the field now attention will be restricted to the behavior of structural glasses that have formed from liquids. We will further restrict attention to glasses that have formed from liquids in which no changes of composition or phase occur during cooling and vitrification. Because this excludes a class of glasses that have become very important in pharmacology and food preservation science, namely the freeze-dried glasses, we will provide a separate section later to deal with the differences that can arise in such cases. The freezing-in of a structural state during cooling of the liquid means that the state of internal equilibrium possessed by the initial liquid is lost. To modernize the classical description, "vitrification," this process has recently (Palmer *et al.*, 1985) been called "ergodicity breaking." This is because states at temperatures above the glass transition satisfy the ergodic hypothesis of statistical mechanics (McQuarrie, 1973) (i.e., systems in equilibrium in the course of fluctuations revisit, or may revisit, the same state within the observation period), hence are called "ergodic states" (usually with the proviso that crystals are excluded). Glasses are "nonergodic."

The definitions given above are both consistent with the latter statement. However, it should be recognized that common usage among physicists is obscuring this distinction. There is a strong tendency to use the term "glassy" for any aspect of a system capable of generating a glass on sufficient cooling. Thus, one sees frequent reference to

1. "Glassy dynamics" – by which is usually meant the dynamics of viscous *liquids* approaching the glass transition temperature from above.
2. "Strong, or fragile glasses" in reference to phenomenology of supercooled liquids above T_g. While such a blurring of the distinction between liquids and glasses is regrettable, it may be inevitable.

The crossover from liquid to glassy (ergodic to nonergodic) behavior occurs over a range of temperature called the "glass transformation range," which is discussed further below. This is inevitable for a kinetically controlled phenomenon, and it is probably inappropriate that the term glass "transition" is used to describe the ergodicity-breaking phenomenon. The term is, however, firmly entrenched, and there is little question of changing it. Because of the range of temperature involved and also because of its dependence on cooling rate, there is a problem in attaching a characteristic "glass transition temperature" to the phenomenon for any particular material. This is compounded when, as is commonly the case, the "glass temperature" T_g is determined during heating because there is then a further (poorly appreciated) dependence on annealing history as well as on heating rate. Nevertheless, when appropriately measure, T_g is very reproducible and has become recognized as an important material parameter. Its assignment is discussed in the following.

The Bartenev empirical equation is valid at not very high cooling rates of glass-forming melts. The generalized equation explains the dependence Tg=Tg(q) over a wide range of cooling rates. The condition proposed by Sanditova *et al.* (2017) for the liquid-to-glass transition can be considered as a modification of the kinetic glass-transition criterion formulated by Schmelzer and his colleagues, and also as an extension of the condition for the transition from a liquid to a glass according to Bartenev.

1   Defining the Glass Transition Temperature

T_g has traditionally been defined (unambiguously, except for measurement difficulties) as the temperature at which the viscosity η of the internally equilibrated supercooled liquid reaches 10^{12} Pa s. The definition is unambiguous because, for a given substance studied at ambient pressure, there is only one temperature at which $\eta = 10^{12}$ Pa s. Its value does not depend on sample history, as for other common definitions discussed below. In inorganic glasses of technological interest, this temperature was observed to correspond more or less to the temperature at which a break in the length–temperature relation for glass rods was observed (due to the higher expansion coefficient α in the ergodic state) (see Bondi, 1967). Partly because this correspondence was totally lost in the case of high polymers and partly because of the simplicity of detection of the "transition" by thermal measurements sensitive to changes in heat capacity, interest then passed to definitions based on differential thermal analysis (DTA) or differential scanning calorimetry (DSC) scans (Moynihan *et al.*, 1976). A case is illustrated in **Fig. 1** for the popular model system, CKN (Moynihan *et al.*, 1976; Rao *et al.*, 1973; Angell *et al.*, 1992; Angell, 1996) (which consists of simple ions in the proportions 40% $Ca(NO_3)_2$ and 60% KNO_3).
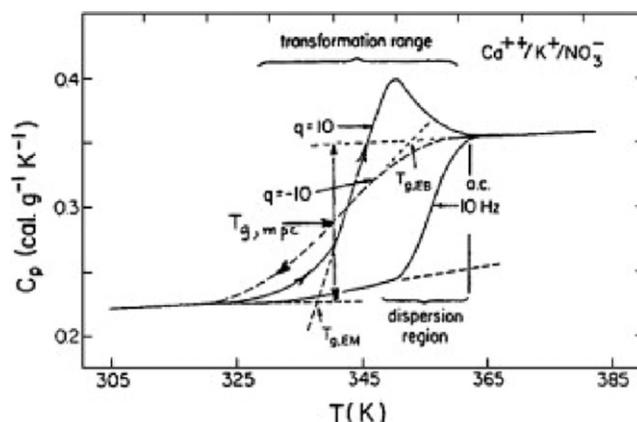
Fig. 1 Heat capacity vs. temperature relations for CKN showing how $T_{g,EM}$, $T_{g,EB}$, midpoint cooling glass temperature, and $T_{g,mpc}$ are defined from heat capacity upscan and downscans, respectively. (Based on original dateMishima, O., 1994. Reversible first-order transition between two H_2O amorphs at -0.2 GPa and -135 K. J. Chem. Phys. 100, 5910 and including estimated a.c. heat capacity dispersion curve at constant frequency of 10 Hz, reproduced by permission of American Institute of Physics from J. Chem. Phys., 1983, 78, 15) which has since been closely confirmed by experiment.) Note that the dispersion range in an a.c. experiment is not usually the same as the transformation range observed in a cooling experiment in which the final state is a glass, i.e., a nonergodic state. In the a.c. measurement, the heat capacity does not depend on the direction of temperature change unless the temperature cycling frequency chosen overlaps the transformation range reciprocal timescale.

The curves in **Fig. 1** are obtained (Moynihan *et al.*, 1976) when the sample is scanned at the standard rate of 10 K min^{-1} during cooling and subsequent heating *without* any "annealing" ("waiting" in spin glass terminology, "aging" in polymer terminology) below T_g.

A commonly used definition of T_g, and the one preferred by the authors for heating scan determinations, is the point marked $T_{g,EM}$ (EM for ergodicity making), which is called the $C_{p,onset}$ definition (Angell, 1996; Wünderlich, 1994). This corresponds to the temperature at which inorganic glasses have viscosities close to the traditional 10^{13} p (10^{12} Pa s) though the viscosities of molecular liquids of low T_g are smaller, e.g., $\sim 10^{10}$ Pa s at this temperature. (Polymers at their $C_{p,onset}T_g$ have higher and often unmeasurable viscosities depending strongly on polymer chain length.) An advantage of this definition is that it is relatively insensitive to prior cooling rate.

Another commonly used definition is the $C_{p,midpoint}$ determined during heating (Wünderlich, 1994), where the viscosity of molecular liquids is only of order $\sim 10^9$ Pa s. It is more sensitive to scan rate and requires the system to be stable against crystallization at any temperature in the transition rate. Each of these temperatures depends on the precise manner in which the system under study was prepared. This is due to the sensitivity of the heat capacity evolution, during heating, to the initial enthalpy of the nonergodic state being heated (Hodge, 1987, 1991).

The only uncomplicated definitions of the glass transition temperature, that are based on changes in thermodynamic properties are those determined during cooling. These avoid any complications arising from thermal history below T_g, and depend only on the cooling rate. Below the use of oscillatory probe methods, such as temperature-modulated DSC, will be discussed that detect a "jump" in heat capacity that, in principle, may also be made independent of thermal history. However, in this case such methods observe the system in the metastable (ergodic) state, and thus belong in the field of relaxation spectroscopy, quite distinct from the temperature-induced ergodicity breaking that has traditionally been at the heart of the glass transition concept.

Examples of downscan definitions of T_g are the volume crossover on cooling advocated by Kovacs (1964) and Plazek *et al.* (1994), the cooling fictive temperature of Hodge (1987, 1991), and the ergodicity breaking (EB) point defined in **Fig. 1** from heat capacity data obtained during steady cooling. For a cooling rate of 10 K min^{-1}, the $T_{g,EB}$ of **Fig. 1** falls at a relaxation time of $\sim 10^{-1}$ s, almost 3 orders of magnitude shorter than the $\sim 10^2$ s characteristic of the normal 10 K min^{-1} C_p onset (or ergodicity-making EM) temperature. Since scanning instruments can now be calibrated during cooling, using liquid crystal mesophase transitions which have negligible hysteresis (Chen *et al.*, 1998; Hensel and Schick, 1997; Menczel and Leslie, 1990), temperature calibration is no longer a problem standing in the way of the downscan measurement.

There are, however, some disadvantages involved in defining T_g during cooling. One is that, for liquids with weak glass transitions, it is difficult to detect. Another is that the downscan definition is unsuitable for systems that can only be obtained in the glassy state by rapid quenching or by other methods that avoid the liquid state entirely. Of these, the first is not too important since most of the interest in the glass transition problem currently is with "fragile" glass-formers which tend to have strong C_p manifestations (Angell, 1991).

The temperature interval $T_{EB}-T_{EM}$, "transformation range," will depend strongly on the liquid character (strong or fragile (Ito *et al.*, 1999)) and it would be better if the downscan T_g could be defined so as to coincide more closely with the common upscan definition. Thus, a preferred choice would be the C_p midpoint temperature of the cooling scan, illustrated in **Fig. 1**, a choice which would correspond closely with the Plazek *et al.* (1994) volume crossover T_g and the Hodge (1987, 1991) cooling fictive temperature. It has been shown in a detailed study of the transformation range in systems of different fragilities (Velikov *et al.*, 2001)

to correspond within 0.5°C with the onset heating definition and the fictive temperature of Tool (1946) and Moynihan *et al.* (1976) for equal 10 K min^{-1} cooling and heating rates. The relation of these (arbitrarily defined) temperatures to a more fundamental glass transition temperature underlying the kinetically determined phenomena, the Kauzmann temperature T_K, is considered elsewhere (Angell, 1997a).

In view of the fact that many theoretical studies of the glass transition are now being made by theorists using computer simulation methods, and of the fact that theorists mostly study phenomena at constant volume, mention should be made of the difference between glass transitions observed in the two cases. In strong liquids (mostly networks with small expansion coefficients), there will be very little difference. In fragile liquids, on the other hand, the expansion coefficient increase at T_g is usually large and the glass transition will be considerably depressed in magnitude. Depending on starting volume, it will also be shifted somewhat in temperature. Some data have recently been reported for the two cases by Colucci *et al.* (1997).

2   The Transformation Range

The "transformation range" is the temperature range needed to change the relaxation time of the system by some 2–2.5 orders of magnitude. In turn, 2–2.5 orders of magnitude of relaxation times is the range needed for the system to pass from fully frozen to fully relaxed, within measurement error. This can be seen from comparison of a scan like **Fig. 1** with the results of equilibrium liquid-state relaxation times, e.g., dielectric relaxation times, made in the same temperature range. For scan rates of 10 K min^{-1}, the onset of the transformation during heating, defined as T_g (onset) in **Fig. 1**, occurs when the relaxation time is 200 s.

For a given system, the temperatures at the beginning and end of the transformation range depend on the timescale of the measurement. The longer the timescale, e.g., the lower the scan rate, the lower the temperature of the transition, and also the narrower the reduced range of temperature, $\Delta T_g/T_g$, over which the change occurs. The narrowing of the transformation range at lower temperatures is due to the fact that the temperature dependence of the relaxation process becomes larger the lower the temperature, according to the Vogel–Fulcher–Tammann equation,

$$\tau = \tau_o \exp[DT_o/(T - T_o)] = \tau_o \exp[F(T/T_o - 1)] - 1 \tag{1}$$

where τ_o, $D = F^{-1}$, and T_o are constants, and τ_o should be $\sim 10^{-14}$ s, a vibration time, for the equation to have physical meaning (Angell, 1997a).

The larger the value of F, the more rapidly the temperature dependence of the relaxation time changes with temperature, and the more "fragile" the liquid is said to be. D is linear in the ratio T_g/T_o, the inverse of which is often used as a measure or fragility. For fragile liquids, studied at the very high cooling rates typical of computer simulations of glass formation, equilibrium is lost in the temperature range in which the temperature dependence of the relaxation time, according to Eq. (1), is very small. In this case the temperature interval covered by the transformation is so broad that it is barely meaningful to talk about a "transition." It covers a range as large as the onset temperature itself, which has led to some confusion in comparison of results of simulation and experiment.

3   Studies Using Oscillatory Perturbations

An additional complication, quite distinct from that due to decoupling of responses discussed above, arises when the detection of the transition from glass to liquid is made by a method using an oscillating stress field.

This applies to most mechanical analysis instrumentation and also to a.c. heat capacity measurements (Birge, 1985; Birge and Nagel, 1986) of which the recently developed thermally modulated differential scanning calorimetry (TMDSC) technique (Reading, 1993; Wunderlich *et al.*, 1994) is a variant. In these cases, when free of effects arising from probe frequencies set too close to the transformation range, the onset of the "liquid-like" property during temperature upscan will not depend on the scan rate but will instead depend on the frequency in use (Birge, 1985; Birge and Nagel, 1986). This is always higher than the $\sim$mHz frequency that corresponds to the onset glass transition temperature enthalpy relaxation time of 200 s ($\tau = 1/2\pi f$). The glass transition temperature can, however, be obtained from such measurements if the frequency of the measurement can be varied. Then, determination of the loss peak temperature for a series of frequencies and extrapolating to the value at 1 MHz yields an onset T_g.

Methods involving the use of oscillating stresses have a distinct *advantage*. When the change from solid-like to liquid-like properties is detected using frequencies more than two decades above 1 mHz (hence above the transformation range), and also at a scan rate slow enough to avoid thermal gradients, the detection is made outside the transformation range, i.e., in the liquid state. This removes all history dependence from the measurement (see the curve marked 10 Hz a.c. in **Fig. 1**). It must be recognized, however, that, in this case, the dynamic mechanical and a.c. scanning calorimetry methods correspond, in principle, with the standard relaxation spectroscopies, such as scanning dielectric relaxation, NMR T_1 relaxation time measurements, and fixed angle Brillouin scattering. For such measurements the temperature at which the change in property is observed as the system relaxes from solid-like to liquid-like behavior should not be called a "glass transition" any more than should the change in dielectric constant observed in a liquid during temperature scanning at a constant electrical field frequency of 100 kHz, or the temperature of the T_1 minimum in NMR relaxation measurements, which are also always made at constant frequency (in the multi-MHz regime). All of

these simply report the temperature at which the relaxation time of the system corresponds to the chosen probe timescale, e.g., $\tau_H = 1/(2\pi \times 10 \text{ Hz})$ for the a.c. scan in Fig. 1. The system itself remains ergodic except with respect to the probe stress, and the temperature detected is only related peripherally to the onset of rigidity on cooling.

To be consistent with the established practice of relaxation spectroscopy, the characteristic temperature should be defined as the temperature of the maximum in the imaginary part of the response (the "loss peak"), but this is often not the case. The definition of the glass transition in TMDSC is usually made at the midpoint in the specific heat rise (the real part of the complex thermal susceptibility). However, TMDSC is a special case because the a.c. frequency applied to the temperature modulation falls within the transformation range. In fact, it is constrained by the various heat flow limitations to be carried out partly within the glass transformation range. This has the effect that two ergodicity-breakings are simultaneously present (one with respect to the scan rate and the other with respect to the modulation).

In TMDSC, this complication is turned to an advantage at the expense of new jargon, as "non-reversing heat flows" are detected. Any source of irreversibility will contribute to the nonreversing heat flow, and separating weak crystallization from enthalpy recovery becomes a challenge. The nonreversing heat flow referred to in TMDSC of ordinary glassformers, is just the TMDSC equivalent of the overshoot seen in the normal DSC scan of Fig. 1, which is determined entirely by kinetic factors. Any factor that makes the enthalpy relaxation more nearly exponential will tend to minimize the overlap of transformation and dispersion ranges and hence reduce such history-dependent effects. The phenomenology of TMDSC has yet to be properly integrated into the field of relaxation spectroscopy though progress is being made (Simon and McKenna, 1997, 2000; Simon, 2001).

Because of the time window restrictions in TMDSC (determined by the thermal energy diffusion time on the one hand, and sample structural equilibration time on the other) it is not possible, as in dynamic mechanical spectroscopy, to acquire data at different frequencies and then to extrapolate to a relaxation time of 200 s to compare with the temperature of the normal calorimetric glass transition (Hodge, 1991, 1994). Rather, the T_g is defined at the midpoint in the C_p rise, and thus depends on the frequency chosen (from within the narrow range available) for the scan. Its relation to the normal T_g thus remains a little uncertain, but it will necessarily be a little higher in temperature, particularly if the onset definition is used for the "normal" T_g. For fragile liquids, whose relaxation times change very quickly with temperature in this range, the difference will not be great.

An additional complication with relaxation spectroscopy definitions of the glass transition temperature is the distinction that must be made between the retardation time and the relaxation time. The first is the time corresponding to the peak in the imaginary part of the frequency-dependent modulus and the second is the peak in the imaginary part of the frequency-dependent susceptibility. The difference can be as high as 2 orders of magnitude in the case of dielectric spectroscopy of high dielectric constant liquids, but is only a factor of 2 or less in the case of enthalpy relaxation. The difference cannot be tested in low-frequency mechanical spectroscopy because of the absence of any finite low-frequency value except in the case of the bulk modulus. Bulk modulus relaxation is more difficult to study, though the work of McKinney and Belcher (1963), which utilized high-pressure equipment, is classic. The development of bulk modulus spectroscopy is in its infancy (Christensen et al., 1997). A factor of 2 uncertainty in the choice of relaxation time (modulus or susceptibility) to compare one response with another corresponds to a difference in defined glass transition temperature of 2–20 K (for T_g near ambient). The uncertainty is smaller the more fragile the liquid.

Some of the same advantages and disadvantages of TMDSC apply to studies made by short step-scanning through the transformation range, as is an option in some current instruments. This technique-development area is interesting but will not be discussed further here.

4   Sample-Related Problems in Glass Transition Detection and Definition

Having dealt with the difficulties in defining T_g that arise from technique, frequency, and modulus versus susceptibility problems, we turn to the difficulties that may arise because of the nature of the sample. The glass transformation range can be broadened and even obliterated for reasons intrinsic to the individual system, which will be discussed here.

It is in the nature of certain glass formers, the nonfragile types, that they have a very small temperature dependence of the relaxation time, i.e., D in Eq. (1) is large. The less fragile the liquid, the wider the reduced transformation range $\Delta T_g/T_g$. This would not be so serious except for the fact that in nonfragile systems the change in heat capacity at the glass transition is small. The reason for this correlation is not yet completely clear but, to the extent that it is real, the problem of defining a glass transition temperature from a scanning measurement of any type is made more difficult. These characteristics (which are general for the nonstructural glasses mentioned in the introduction) are common to many of the high silica glasses of optical and ceramic technology. This is one reason why the glass transformation range was traditionally defined in terms of glass former viscosity. The 10^{13} p viscosity definition of T_g permeates the glass science literature, though the viscosity of molecular liquids is generally much smaller, and the difference increases with liquid fragility. For fragile inorganic glass formers of high T_g, 10^{13} p at the onset T_g seems to hold within an order of magnitude. This problem has reappeared for the case of amorphous water (Ito et al., 1999), which, due to its tetrahedral network structure, behaves like a very strong liquid.

For systems whose transformation ranges are very broad due to their multi component nature, structural inhomogeneity, and ill-defined state of structural arrest in the glassy state (absence of a single fictive temperature), the problem of defining a glass transition that will satisfy a broad community becomes problematic, even insurmountable. The absence of a well-defined internally equilibrated state at *any* temperature in many systems of interest is an additional and irresolvable complication.

Unfortunately, the foregoing describes the situation with many of the most actively researched amorphous materials. These are the materials of the food science industry and many of the complex formulations of the pharmaceutical sciences, for which the use of the structurally slowed-down or arrested state is becoming of major importance as a means of preserving the important components of the "glass."

The best that can be done in such cases is to define the temperature at which the fastest component of the system is arrested (for a measurement on some agreed-upon timescale). According to our earlier discussion, the fastest components will be those relaxed by movement of the water molecules. The best method for characterizing their slowdown is probably the mechanical modulus relaxation, since the calorimetric strength of the relaxation is likely to be weaker and more variable. The measurement by scanning calorimetry, on the other hand, is so much simpler from a sample preparation standpoint that it is unlikely to be replaced. In this case, observability of significant events will be aided by adoption of a slow-cool/fast-heat measurement protocol. This is a signal enhancement technique that cannot be utilized with an ergodic sample a.c. heat capacity measurement (frequency >1 Hz) but may be viable in TMDC. In biosystems, slow-cool/fast-heat protocols may often result in the generation of a prepeak (see next section), which will be easier to detect than a very gradual increase in heat capacity. As mentioned earlier, the anneal-and-scan method, which is equivalent to a very-slow-cool, fast-heat protocol, can be used to show the existence of a hierarchy of relaxation processes, extending at least to the denaturation temperatures of the proteins in such systems (Sartor et al., 1994). These measurements also permit the assessment of relative strengths of the relaxation processes occurring in a given temperature range.

5   Techniques to Determine Transition Temperature and Relaxation Time

The glass transition temperature of highly cross linked polymers are estimated by an improved method of thermomechanical tests (Kryzhanovskii et al., 2012). The distinctiveness of thermomechanical tests of the polymers are analyzed. The physical interpretation of their glass transition temperature as a boundary region between predominantly glassy and highly elastic states is validated. The thermomechanical tests allow construction of tangent lines and consideration of plastic deformation occurring during the testing procedure.

Differential scanning calorimetry (DSC) is combined with thermo stimulated depolarization currents (TSDC) to determine relaxation times of bisphenol A polycarbonate around the glass transition temperature (Delbreilh et al., 2009). These assessments are performed using samples with different thermal histories below and above the vitrification transformation. This method enables the extension of the range of equilibrium relaxation times measured by dielectric spectroscopy. By this procedure recalculation of the values of the Kauzmann temperature and fragility index is possible.

The relaxation spectrum of rapidly quenched $Mg_{65}Cu_{25}Y_{10}$ metallic glass ribbons is examined by mechanical spectroscopy at temperatures below and around the glass transition (Pineda et al., 2013). The comparison between hyper-quenched and relaxed samples is used to investigate the origin of the low temperature "excess wing" of internal friction usually observed in mechanical spectroscopy of metallic glasses. The findings show that the excess wing can be attributed to access of the system to the broad relaxation process while indication of secondary relaxations is not found. This implies that in this glassy system the activation energies of structural relaxation and low temperature deformation are directly related to the activation energy of the main relaxation process of the glassy state.

The glass transition of Cyclodextrin polymer was located above the thermal degradation point and making the direct measurement of glass transition temperature difficult (Tabary et al., 2016). However, the virtual glass transition temperature could be estimated by mixing these polymers with different plasticizers which reduces the glass transition temperature sufficiently to make the glass transition observable.

Differential Scanning Calorimetric (DSC) measurements of $Se_{58}Ge_{42-x}Pb_x$ ($9 \leq x \leq 20$) glasses show single glass transition and double crystallization, which indicate the development of phase separation in the samples (Deepika and Saxena, 2010). The phases present in the samples were examined using XRD. The kinetics of the glass transition has been investigated in terms of the variation of glass transition temperature with composition and heating rate. In addition to this, activation energy of the glass transition (E_t) has also been evaluated and its composition dependence is also investigated. The thermal stability of these glasses has been investigated using various stability criteria: Deiztal first glass criterion, ΔT, Saad and Poulain weighted thermal stability, H^i and the S-parameter. The values of these parameters were acquired using various characteristic temperatures such as the glass transition temperature, T_g, the onset temperature of crystallization, T_c, and the peak crystallization temperature, T_p. The values of stability parameters reveal that the phase corresponding to second crystallization is more stable than the phase corresponding to first one. The stability in terms of the lead (Pb) content has been determined considering the values of stability parameters of the phase corresponding to second peak. It was found that the stability increases with the lead content.

6   Modeling the Glass Transition

For the simpler type of system, illustrated in Fig. 1, the variations in time-dependent specific heat observed through the glass transition during cooling and heating (and also for arbitrary time temperature histories) can be reproduced rather well by phenomenological models that take into account the three canonical aspects of relaxing liquids. These are the non-Arrhenius nature of average relaxation time, the nonexponentiality of relaxation process, and the nonlinearity (or sample state dependence)
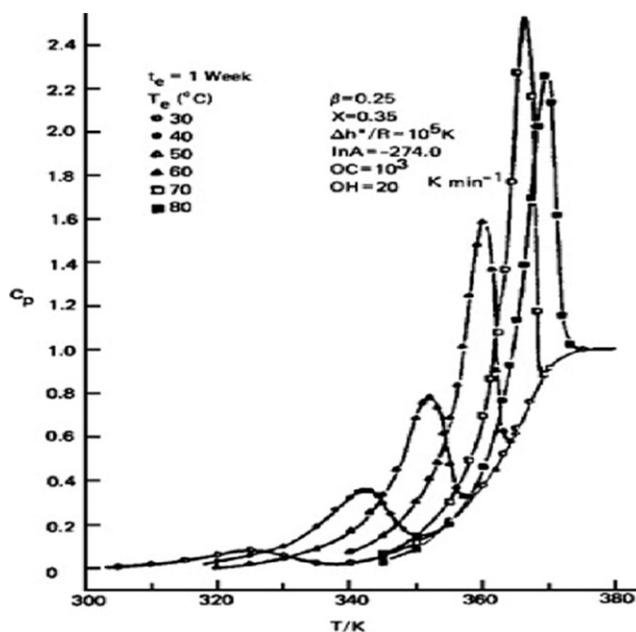
Fig. 2 Variation of the apparent heat capacity with increasing temperature during a 10 K min^{-1}. Upscan, after annealing one week at different temperatures below the normal T_g (as listed in diagram), according to the TNM phenomeological model with parameters indicated in the diagram. Note the "annealing prepeak" which appears for low-temperature anneals. This feature is more pronounced the less exponential the isothermal relaxation function (stretched exponential β parameter) and the more rapid the initial cooling rate. Experimental data are for polystyrene (reproduced by permission of American Institute of Physics from Phys. Rev. Lett., 1997, 79, 1317).

of the relaxation process. Three models are in common use: KFAR (Kovacs *et al.*, 1979); TNSM (Moynihan *et al.*, 1976); and SH and their detailed applications are described in Scherer (1986) and Hodge (1991, 1994). A review of the whole field has been given by Hodge (1994), Simon and McKenna (2000) and Angell *et al.* (2000). An important aspect of the models is their account of the way in which an endothermic "prepeak" can emerge in ordinary liquids subject to fast cooling followed by slow heating, or on scanning after prolonged annealing at an appropriate temperature. This is a direct consequence of the nonexponentiality of the relaxation process. The phenomenon and its modeling are displayed in **Fig. 2**, taken from Hodge and Berens (1982) and Hodge (1987). The prepeak phenomenon can become the dominant feature of DSC scans in highly nonexponential systems, hence is to be expected, and is frequently seen in the DSC scans of biosystem samples (Belliveau *et al.*, 1992; Ablett, 2001).

A model was established for the time dependent behavior of glass transition of amorphous networks (Xiao *et al.*, 2013). This thermomechanical constitutive model used multiple discrete relaxation processes to illustrate the distribution of relaxation times for stress relaxation, structural relaxation and stress activated viscous flow. Deformation programming, storage and deployment for shape memory polymers can happen in a narrow range around glass transition temperature. This is valid for many proposed shape memory polymer biomedical devices, where the activation temperature is tailored to be around 40°C (body temperature) and device storage is expected to be around 20°C. The programming strategies for improving the recovery rate and actuated have been identified by modeling the shape memory behavior. This model could help overcome challenges in the design of shape memory polymers.

A novel approach to clarifying the hole activation model of a viscous flow of glass forming liquids is proposed (Sanditov, 2010). This model explains the concept on the exponential temperature dependence of the free energy of activation of a flow within the range of the liquid–glass transition in total agreement with available experimental data. The "establishment of a fluctuation hole" in high heat glass forming melts is considered as a small scale low activation local deformation of a structural network. The quasi lattice necessary for the switching of the valence bond is the main elementary event of viscous flow of glasses and their melts. In this sense, the hole formation is a conditioned process. A remarkable increase in the activation free energy of viscous flow in the liquid–glass transition region is explained by a structural transformation that is reduced to a limiting local elastic deformation of the structural network, which, in turn, originates from the excitation of a bridging atom like the oxygen atom in the Si-O-Si bridge. At high temperatures, an essential amount of excited bridging atoms always exists, and the activation free energy of viscous flow is almost independent of temperature. The hole activation model is closely associated with a number of well known models describing the viscous flow of glass forming liquids.

7   Thermodynamic Relations at the Glass Transition

The heat capacity is, of course, not the only derivative thermodynamic property that "jumps" at the glass transition. Any property whose value is determined by fluctuations about the equilibrium state will show a jump, spread out across the transformation

range. Because such fluctuations may be uncorrelated, the jumps observed for different properties may differ considerably in magnitude, and may even differ is sign. For instance, in their discussion of fluctuations, Landau and Lifshitz (1958) demonstrated that the compressibility is determined by the mean square fluctuation in the volume, according to

$$k_T = (\Delta V)^2 / V k T \tag{2}$$

while the heat capacities are related to the kinetic energy fluctuations,

$$C_v = K T^{2/} / (\Delta T)^2 \text{(at constant volume)} \tag{3}$$

and the entropy fluctuations,

$$C_p = (\Delta S)^2 k \text{(at constant Volume)} \tag{4}$$

The similarity of the changes in heat capacity C_p, expansivity α, and isothermal compressibility, κ_T, seen at the glass transition, and those expected in Ehrenfest second-order transitions has naturally prompted enquiry about the validity of the two Ehrenfest equations for the pressure dependence of the transition. Such a possibility is not necessarily in conflict with the fact that the observed glass transition is certainly not a *thermodynamic* transition. Davies and Jones (1953b) demonstrated that a sufficient condition for validity of these equations would be that the quantities S_{ex} and V_{ex}, measured relative to some well-defined reference state such as the crystal, stay the same irrespective of the pressure at which the system goes through the transition. Following Davies and Jones, the Ehrenfest equations take the forms:

(from the condition V_{ex}=constant at T_g)

$$dT_g/dP = \Delta k / \Delta \alpha \tag{5}$$

and (from the condition S_{ex}=constant at T_g)

$$dT_g/dP = V T \Delta \alpha / \Delta C_p \tag{6}$$

The validity of Eqs. (5) and (6), when T_g is measured at the same rate at each constant pressure, may be seen as a test of the validity of theories that propose that the glass transition is a consequence of diminishing "excess" or "free" volume on the one hand or "excess entropy" on the other. If these excess quantities were both determined by the same single order parameter, then both equations would be valid, and the Prigogine–Defay ratio obtained by combining Eqs. (5) and (6) would be unity. The relations have been tested by a number of workers over the years, and Eq. (6) has been found to hold within experimental error in almost all cases. Eq. (5), on the other hand, fails regularly (Goldstein, 1973; Moynihan and Lesikar, 1981).

A direct test of the constancy of S_{ex} at the glass transition has been made by Takahara and co-workers (Takahara et al., 1994) for the compounds, 3-methyl pentane and 1-propanol. These workers found that S_c is only approximately constant and that the combination TS_{ex} is much more nearly a constant quantity. Interestingly, this is the prediction of the Adam–Gibbs entropy theory (Adam and Gibbs, 1965). For a constancy of the TS_c product at the glass transition, the equivalent of the second Davies–Jones relation is

$$dT_g/dP = V T \Delta \alpha / S_c + \Delta C_p \tag{7}$$

This has been tested for the case of $ZnCl_2$ and found to be superior to Eq. (6) (Williams and Angell, 1977). It is only for systems with relatively small values of ΔC_p that the difference would be expected to be discernible within experimental error.

The relation between thermodynamic quantities has been and continues to be a source of dispute and the reader should refer to Nieuwenhuizen (1997) and Speedy (1999) for viewpoints that differ from the traditional views expressed above. The relation between the magnitudes of the various jumps in derivative thermodynamic properties obtained by combining Eqs. (5) and (6) is known as the Prigogine–Defay ratio $\prod$. It is

$$\prod = V T \Delta \alpha^2 / \Delta \kappa \Delta C_p \to 1 \tag{8}$$

The equality can hold only if the state of the system is determined by a single order parameter, which is never true in the case of a grass transition.

8   Supplementary Glass-Like Transitions

The occurrence of sub-T_g relaxational jumps in thermodynamic properties or tensile moduli due to "fast" particles in the glass was mentioned earlier. A quite different phenomenon arises in systems in which either:

1. The molecules have internal structural degrees of freedom that can be excited above the normal glass temperature; or
2. there are two very distinct types of interparticle interactions acting in the system.

In each of these cases a supplementary increase in heat capacity can occur well above the normal calorimetric T_g as the extra degrees of freedom become excited (Angell, 1997b). These may show scan-rate-dependent properties that are related to those of the ordinary glass transition, but which now appear in the fluid liquid state or the plastic crystal state. These are of interest not only as novel relaxational phenomena, but also for the way in which they might vary with increasing complexity, forming a hierarchy with the protein unfolding/refolding phenomenon (Angell, 1999).

The first of these was seen in the plastic crystal state by Seki and co-workers (Kishimoto et al., 1978) for the molecule $(CFCl_2)_2$ and was identified in great detail with the configurational excitation obtained by rotation about the C–C bond to form the higher-energy structural isomer of the molecule. It is therefore an intramolecular excitation. This also seems to be the case for the extra glass-like jump in heat capacity seen in the case of isocyanocyl cyclohexane (Kishimoto et al., 1991) in which a boat–chair conversion occurs. A similar, but stronger, phenomenon occurs in the *liquid* states of the sugars, fructose and galactose (Fan and Angell, 1996), at temperatures well above the "normal" T_g at which the liquids become brittle solids. It has been interpreted as being due to the furanose–pyranose anomer exchange equilibrium (Fan and Angell, 1996), for which the thermodynamic parameters are such as to make $K_{eq} = 1$ in the metastable liquid range at temperatures between T_m and T_g. Again, scan rate-dependent and annealing phenomena, easily confused by the unwary for glass transitions, are seen.

Intermolecular examples of this type of supplementary transition are now being found in some liquids of hydrogen-bonded molecules (Alba-Simionescu et al., 1999). In these, the hydrogen bonds remain intact through the normal glass transition (which involves thermal excitation of weaker van der Waals interactions) but begin to break (with the absorption of energy) at higher temperatures.

While such phenomena seem to be uncommon in pure liquids, they are likely to be more common in binary and multi-component solutions – in which they will simply be classified as diffusion-controlled chemical reactions. Whatever their classification, the potential for confusion with glass transitions exists and must be guarded against.

9   Freeze-Dried and Other "Composition-Quenched" Glasses

We earlier excluded, from our description, glasses that have been prepare via change of composition. These include the now widely studied freeze-dried glasses, as well as those formed isothermally by solvent evaporation, polymerization reactions, and liquid–liquid phase separation near T_g. All of these require diffusion of molecular species over distances large with respect to the molecular diameter to equilibrate. For equal diffusivities, the composition fluctuations about the equilibrium state in such systems must therefore occur on longer timescales than the structural fluctuations determining the ordinary glass transition since the latter only require motions over fractions of the molecular diameter (Angell, 1991). During steady cooling, therefore, a system will become arrested with respect to the composition fluctuations at a different and higher temperature than that of the ordinary glass transition (Laberge et al., 1973). Differences in properties have been discussed for the freeze-dried glass case (Shamblin et al., 1999) for the polymerization vitrification case (Tombari and Johari, 1992); and for the liquid–liquid phase separation case (Laberge et al., 1973). They are not large but, since they complicate an already complex phenomenology, they are not considered further here.

10   Conclusions

Glasses are disordered materials that behave mechanically like solids but lack the periodicity of crystals. Glasses are traditionally made by cooling a viscous liquid fast enough to avoid crystallization. Although this super cooling process is well known for decades, the molecular processes by which liquids acquire amorphous rigidity upon cooling and glass transition are not fully understood. Glass transition continues to draw research attention in molecular physics, material science and chemistry. This article is devoted to reviewing the characteristics of glass transition, definition and determination of glass transition temperature and thermodynamics in glass transition. The recent developments in the modeling of glass transition are also presented.

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