

CALORIMETRIC MEASUREMENTS OF THE GLASS TRANSITION

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ABSTRACT

The problems related to the measurement of heat capacity near and within the glass transition region are analysed taking into account the irreversibility inherent in the production of a glass. A brief review of both the main theories of the glass transition and the possible ways to minimize irreversibility on going through the glass transition are presented. The possibility of evaluating the entropy production from the measured apparent heat capacity is outlined.

INTRODUCTION

The glass transition is generally observed in both organic and inorganic substances making it plausible to assume that it is a universal phenomenon. It is well defined experimentally and it is seen by the occurrence of characteristic rounded discontinuities of, for instance, specific heat, compressibility and thermal expansion at the glass transition temperature, T_g . The physical origin of these discontinuities is the "freezing" of the liquid diffusive atomic motion. However, the glass transition continues to be an enigmatic feature of the glassy state in spite of the several attempts made in the literature to model the transition theoretically.

The glass transition is very often measured by a thermal analysis method such as differential thermal analysis (DTA) or differential scanning calorimetry (DSC). Such methods allow the measurement of the glass transition temperature and the apparent heat capacity of the sample (1,2). In this paper the connection between the apparent heat capacity of the glass through the glass transition and its true heat capacity will be discussed.

THEORIES OF THE GLASS TRANSITION

If the heat capacity of the liquid is higher than that of the crystal (as is usual in glass forming liquids) there will be a temperature, T_0 , below which the entropy of the liquid will become less than that of the crystal. As first stated by Kaufmann (3) it is unlikely that this will ever occur and therefore the heat capacity of the liquid has to decrease at a temperature above T_0 . This is exactly what happens at the glass transition so it may be a thermodynamic phenomenon. Various models have been proposed with the underlying idea that

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glass transition is a thermodynamic phase transition. Among them is the theory developed by Gibbs and coworkers (4,5) wherein the configurational entropy of linear molecular chains was related to the viscosity. The experimental T_g in this theory is directly related to the falling out of equilibrium of the system at low values of configurational entropy, because attainment of different configurational states requires a high degree of cooperativity. In another approach Goldstein (6-8) has considered three main contributions to the excess "configurational" specific heat of liquids above glass transition, namely, the molecular rearrangement processes and the changes in both lattice frequencies and in nonharmonicity due to these structural rearrangements. Below glass transition the excess specific heat of the glass relative to the crystalline material is very small as compared with the liquid, and it is mainly due to both the differences in the vibrational properties between the glass and the crystal and to the relaxation occurring below glass transition. Another approach to glass transition is the free volume theory (9-12) that emphasizes the concomitant decrease in volume and fluidity of glass-forming melts in the supercooled region. The slowness of molecular transport in liquids is attributed to a scarcity of free volume rather than to the existence of energy barriers. The main origin of the glass transition in this theory is a contraction of the free volume down to a limiting value. Below this critical value of the free volume the particle transport is considered to be impossible. The theory has been extended recently (13,14) incorporating ideas from percolation theory. In a basically different approach Angell and Rao (15) discussed glass transition using concepts of the Ising model developed for crystalline phase transitions. They abstracted a lattice of bonds from the non-periodic glass structure and considered the consequences of excitation of bonds. An appropriate concentration of such broken bonds around a particle would give rise to the familiar transport.

APPLICABILITY OF THERMODYNAMICS TO THE GLASS TRANSITION

A liquid which has been undercooled to a temperature between the melting point and glass transition is in a metastable state of equilibrium. In most experiments this state is found to be independent of previous history, so that it is well defined in terms of the usual thermodynamic state variables (16). Thus it can be stated that above glass transition the relaxation times for molecular degrees of freedom are very short compared to the experimental time scale. Now, it is said that a liquid has gone through a glass transition on the way to the final temperature T if at T it behaves like a solid on all feasible experimental time scales. This means that the glass in a metastable state may exist because below T_g the relaxation times for molecular rearrangements are much longer than the time scale of the measurement process and the structural arrangements are essentially frozen-out. In that sense, the observed changes of thermodynamic properties at T_g can be qualitatively explained by the transition from an ergodic system, the melt, to a non-ergodic one, the glass (17-20). Therefore, at constant pressure the temperature axis may be divided (18) into the region of the undercooled liquid, the region of the glass and the intermediate glass transition region. The limits of the glass transition region depend on the experimental process of cooling or heating but they are reasonably well defined in general because of the rapid temperature dependence of the molecular relaxation times.

The problem faced with glass transition is that of irreversibility. In the glass transition the change of entropy can be split into two terms

$$dS = d_m S + d_i S$$

where $d_m S$ is the measured entropy change due to the exchange of heat with the surroundings, and $d_i S (\geq 0)$ is the creation of entropy not provided by external exchange. If the system exchanges only heat and volume with its surroundings, the internal and external pressures remain equal, and pressure and temperature are homogeneous in the material all the time, then the creation of entropy $d_i S$ will be given by

$$T(d_i S/dt) = - (dG/dt) - S (dT/dt) \geq 0$$

Here S is the entropy, G the Gibbs free energy, T the temperature and t time. Following Cunat and Hertz (21) the previous relation can be written as follows

$$(T/S)(d_i S/dt) = - (1/S) (dG/dt) - (dT/dt) \geq 0$$

and may be illustrated as in figure 1.

This method of representation, when the temperature axis is included, allows the understanding of how the irreversibility occurs on cooling the liquid. This is shown in figure 2. Assuming that the liquid is initially at temperature T_a , during a rapid quench the path followed by the system in the space $(T, (dT/dt), (1/S)(dG/dt))$ (figure 2a) or in a two-dimensional projection (figures 2b & 2c) is given by curve ABC contained in the reversibility plane. At the particular stage C it intercepts the upper limit of the glass transition region and from there the rate of change of temperature is too rapid compared to the slowest processes for structural rearrangement. So the system leaves the reversibility plane and enters the irreversibility domain. In figure 2 it is assumed that in the limit of zero cooling rate the extent of the glass transition region will approach zero, and that this will happen at temperature T_0 . As outlined before there is no definitive theoretical proof of this and no experimental proof can be obtained from direct measurement, because as the cooling rate decreases the sensibility of the measurement of glass transition also decreases. However, as long as the system remains in the glass transition region there is an entropy production and so it is in this region that recovery or relaxation processes may occur. If we call ΔS the true entropy change of the system on heating through the glass transition region, its relation with the measured apparent entropy change $\Delta_m S$ is given by

$$\Delta S \geq \Delta_m S = \int \frac{C_{p,app}}{T} dT$$

The difference $\Delta S - \Delta_m S$ is the entropy production, ΔS_i , and $C_{p,app}$ is the apparent heat capacity measured (for instance in DSC). In the glass transition region $C_{p,app}$ does not coincide with the true heat capacity of the material. Jackle (18) gave an estimate of the entropy uncertainty through the glass transition as

$$|\Delta S_{unc}| \leq \frac{1}{2} C_p(T_0) (T/T_0)^2$$

where T is the width of the glass transition region. Unfortunately, $C_{p,app}$

changes continuously with temperature making it difficult to fit experimentally the limits of the glass transition region (especially for most metallic glasses).

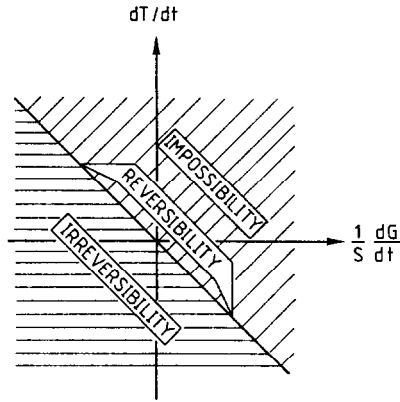


Fig. 1.- Schematic diagram showing the irreversibility domain and the reversibility line.

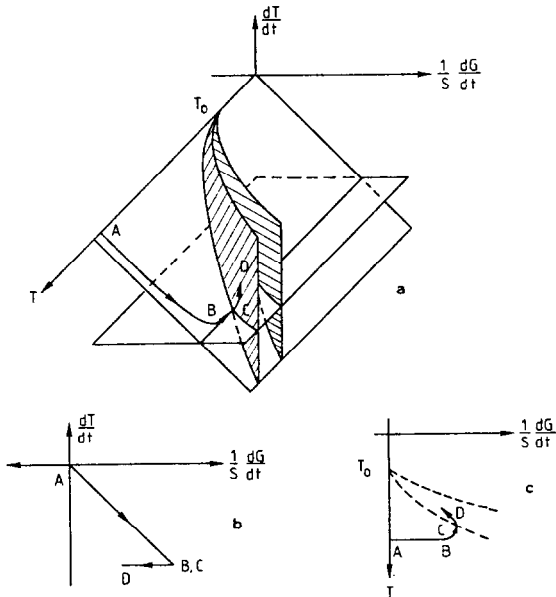


Fig. 2.- Schematic representation of a cooling experiment. a) In a three dimensional space; b) and c) in two dimensional space.

To rid the apparent heat capacity of its irreversible contribution Xu and Ichikawa (22) proposed to use instead of $C_{p,app}$ a "pseudostep function" given by

$$C_{p,app} \left| \begin{array}{ll} C_{p,g}(T) & T < T_f \\ C_{p,l}(T) & T > T_f \end{array} \right.$$

where the subscripts *g* and *l* refer to the glass and supercooled liquid, respectively. The fictive temperature, T_f , introduced by Davies and Jones (16) is that temperature at which a glass would be found in equilibrium with the liquid if brought there from its actual state sufficiently quickly to avoid relaxation to occur. In general, the overall apparent heat capacity versus temperature curve shifts to higher temperature on increasing the heating rate (23). As a result, both T_g and T_f "apparently" increase with heating rate.

When the glass can be cycled through the glass transition region without crystallizing it, the total entropy production in a cycle may be measured. The usual $C_{p,app}$ and S_{app} versus temperature curves obtained on heating and cooling an as-quenched glass through the glass transition region are shown in figure 3. Curves *b* and *c* form a closed path and the total true entropy change related with this path is zero. Therefore, the total entropy production may be evaluated and it is given by

$$\oint d_i S = - \oint \frac{C_{p,app}}{T} dT \geq 0$$

Measurements of this quantity in a Ge-Sb-Se-Te glass (24) gave a value ≤ 0.03 J/K g-at (which was the accuracy of the measurement) indicating that the cycle runs without "relaxation" in that particular experiment, but a greater degree of irreversibility is indeed possible. As far as $\Delta_i S$ in a cycle is different from zero, the apparent heat capacity measured differs from the true heat capacity of the sample.

To avoid most of the irreversible part in the apparent heat capacity measured through the glass transition region the better practical solution is to heat-treat the as-prepared glass. The "standard procedure" (25-29) is as follows. The as-prepared glass is heated up to a temperature high enough to get almost internal equilibrium but low enough to remain below the crystallization temperature. Then it is cooled at a moderate scan rate (say 20-80 K/min) to the temperature at which measurements will begin. As a consequence of this preliminary heating of the glass within the glass transition region the heat capacity measured by DSC or the thermal behaviour recorded in DTA become almost insensitive to the initial melt quenching rate. As an example figure 4 shows the apparent heat capacity relative to that of the crystalline material, ΔC_p , for a $Fe_{40}Ni_{40}B_{20}$ metallic glass (28). Curve *a* gives the value obtained for a non-treated sample and curve *b* for a sample previously heated up to 680 K and then cooled down to 400 K at a rate of 80 K/min. The non-treated glass has an irreversible exothermic peak which has completely disappeared in the heat-treated glass.

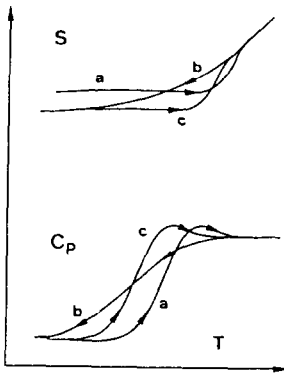


Fig. 3.- Schematic S and C_p curves on heating and cooling through the glass transition. a) First heating of an as-quenched glass; b) cooling and c) reheating the same glass.

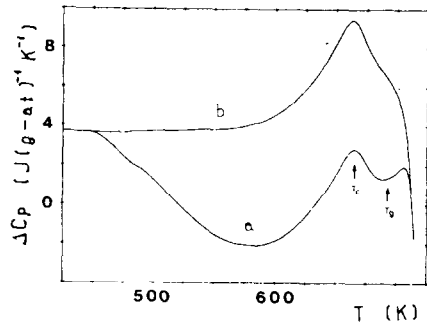


Fig. 4.- ΔC_p of a $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ metallic glass: a) non-treated sample; b) heat-treated glass (previously heated to 680 K and then cooled to 400 K at a rate of 80 K/min).

CONCLUSIONS

The major difficulty inherent in the calorimetric measurements of the glass transition phenomena is the irreversibility of the process. This irreversibility prevents the identification of the apparent heat capacity measured for the sample with its true heat capacity. We have outlined the difference between the measured entropy change due to the exchange of heat with the surroundings, as obtained from the apparent heat capacity, and the total change of entropy which includes the entropy production. A significant decrease of this entropy production can be realised by a previous heat treatment of the sample. We have mentioned the ways proposed in the literature to estimate the uncertainty of the entropy for the glass and to rid or to minimize the apparent heat capacity of its irreversible contribution. Finally, we have pointed out how to measure the entropy production on going through the glass transition within a closed path beginning and ending in the liquid state.

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